THERMAL AND PHOTOCHEMICAL STUDIES OF 9,10-BIS(TRIFLUOROETHENYL)PHENANTHRENE AND PERFLUORO-*E,Z,E*- AND *E,E,E*-4,5-DIMETHYL-2,4,6-OCTATRIENE AND THERMAL STUDIES OF TERMINALLY FLUORINATED 1,5-DIENES

By

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TO DAD, MOM, JACQUELINE, HELEN AND KARYN

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A complete list of all of the friends I am indebted to for assisting me to this point would require a dissertation in itself. Hopefully in this short space I can give justice to a few, with the many not mentioned being assured that they will always be in my thoughts.

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Abstract of Dissertation Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
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THERMAL AND PHOTOCHEMICAL STUDIES OF 9,10-BIS(TRIFLUOROETHENYL)PHENANTHRENE AND PERFLUORO-*E,Z,E*- AND *E,E,E*-4,5-DIMETHYL-2,4,6-OCTATRIENE AND THERMAL STUDIES OF TERMINALLY FLUORINATED 1,5-DIENES

By

Keith W. Palmer

August 1993

Chairman: William R. Dolbier, Jr.
Major Department: Chemistry

Thermolysis of 9,10-bis(trifluoroethenyl)phenanthrene was examined in solution between 140°C and 193°C, and led to formation of 1,2,2,3,3,4-hexafluoro-2,3-dihydrotriphenylene and 1,4,4,5,6,6-hexafluoro-2,3-(9,10-phenanthro)bicyclo[3.1.0]hex-2-ene by irreversible, competitive first-order processes. The competitive formation of 1,4,4,5,6,6-hexafluoro-2,3-(9,10-phenanthro)bicyclo[3.1.0]hex-2-ene is virtually unprecedented in 1,3,5-triene thermal chemistry with only one similar cyclization found in the hydrocarbon literature. Thermolysis of 1,4,4,5,6,6-hexafluoro-2,3-(9,10-phenanthro)-bicyclo[3.1.0]hex-2-ene led to further rearrangement and was examined in solution between 180°C and 193°C. This material was found to rearrange to 4-difluoromethylidene-3,3,5,5-tetrafluoro-1,2-(9,10-phenanthro)cyclopent-1-ene

and 1,2-(9,10-phenanthro)-3,5,5-trifluoro-4-trifluoromethyl-1,3-cyclopentadiene through irreversible, competitive first-order processes.

Photolysis of 9,10-bis(trifluoroethenyl)phenanthrene in solution led to 1,4,4,5,6,6-hexafluoro-2,3-(9,10-phenanthro)bicyclo[3.1.0]hex-2-ene as the major product with 1,2,2,3,3,4-hexafluoro-2,3-dihydrotriphenylene and [2π+2π] cycloaddition products 1,4,5,5,6,6,-hexafluoro-2,3-(9,10-phenanthro)-bicyclo[2.1.1]hex-2-ene and 1,4,5,5,6,6-hexafluoro-2,3-(9,10-phenanthro)-bicyclo[2.2.0]hex-2-ene being observed in minor amounts.

Thermolysis of perfluoro-*E,Z,E*- and *E,E,E*-4,5-dimethyl-2,4,6-octatriene was studied in solution between 154°C and 202°C and initially found to undergo C4-C5 double bond isomerization. At higher temperatures, an equilibrium between the perfluorooctatriene and perfluoro-*cis*- and *trans*-1,3,4-trimethyl-4-(*E*-1-propenyl)cyclobutene is established requiring an 4π electron, conrotatory electrocyclic process.

Photolysis of perfluoro-*E,Z,E*- and *E,E,E*-4,5-dimethyl-2,4,6-octatriene in solution leads to formation of perfluoro-*trans*-2,3,5,6-tetramethyl-1,3-cyclohexadiene by a 6π electron, conrotatory electrocyclic process. This material was found to undergo further photo-cyclization to perfluoro-*trans*-2,3,5,6-tetramethylbicyclo[2.2.0]hex-2-ene through a 4π electron, disrotatory electrocyclic process.

Reluctance of these perfluorinated-1,3(*Z*),5-trienes to undergo the thermal, 6π electron, disrotatory electrocyclization *via* the required boat transition state was evident, as was the facility of the photoprocess to occur through the photo-allowed 6π electron, conrotatory electrocyclization *via* a chair transition state. This disparity was believed to arise from a detrimental interaction between terminal *cis* fluorines as the 1,3(*Z*),5-triene approaches the boat-like disrotatory transition state and required further study.

The system chosen to probe this effect was the thermal [3,3]-sigmatropic rearrangement of terminally *gem*-difluorinated 1,5-dienes. Synthesis and gas phase thermal study of 1,1,6,6-tetrafluoro-1,5-hexadiene, 1-difluoromethylidene-4-methylidenecyclohexane, 1,4-di(difluoromethylidene)cyclohexane, and solution phase thermal study of *meso*- and *d,l*-1-(2-difluoromethylidenecyclopentyl)-2-difluoromethylidenecyclopentane, were carried out and the transformations found to occur by well-behaved, irreversible, first-order processes to the respective [3,3]-shift products. Comparison of the measured activation parameters for these processes and values for the corresponding hydrocarbon and partially fluorinated 1,5-dienes from the literature indicates that terminal *gem*-difluorination accelerates thermal processes occurring through chair transition states while inhibiting processes occurring through boat transition states.

CHAPTER 1

AN OVERVIEW OF FLUORINE SUBSTITUENT EFFECTS IN ORGANIC SYSTEMS

Introduction

The isolation of fluorine by Henri Moissan on June 26, 1886, created considerable academic interest, and led to rapid advances in the field of fluorine chemistry.[1] In 1930, Midgely and Henne developed CF_2Cl_2 as a cheap and safe refrigerant to replace the toxic gas ammonia which elevated fluorine chemistry out of it's status as an academic novelty and initiated the organo-fluorine industry. Due to the Manhattan Project and nuclear energy applications in the early 1940s, large scale production of elemental fluorine became necessary. The post-World War Two era saw intense interest in organo-fluorine chemistry develop in industrial and academic sectors. This interest was primarily due to the fascinating properties exhibited by fluoroorganic materials developed during the concentrated research directed towards production of the atomic bomb. Fluorine exhibits remarkable effects when utilized as a substituent in organic systems and a variety of factors intrinsic to the fluorine atom are responsible. The purpose of this introduction is to address factors which will be pertinent within this current study by reviewing fluorine effects in a series of simple and well characterized organic systems.

The effects exhibited by fluorine as a substituent are due to three intrinsic characteristics of the fluorine atom; extreme electronegativity, non-bonded electron pairs, and small relative size. Fluorine is the most electronegative of all

elements with a Pauling scale value of 4.10 as compared with oxygen (3.50), chlorine (2.83), bromine (2.74), carbon (2.50), and hydrogen (2.20).[2] Strong polarization of fluorinated molecules through the σ bonding framework and through space (field effects) are results of fluorine's large electronegativity. The atom is mono-valent and accommodates three non-bonded electron pairs in orbitals of similar dimension to hybridized orbitals on carbon.[3] Because of these two preceding factors, fluorine exhibits an interesting donor/acceptor contradiction under certain circumstances in that the strong removal of electron density from a bound atom can be offset due to back donation of density from the non-bonded electrons. The van der Waals radius of fluorine is 1.47 Å.[4] Compared with the other halogens, carbon, and hydrogen (van der Waals radii: Cl, 1.73 Å; Br, 1.84 Å; I, 2.01 Å; $C_{aliphatic}$, 1.70 Å; H, 1.20 Å),[4] fluorine should exhibit minimal spatial requirements as a substituent, a fact which has allowed for complete substitution of hydrogen by fluorine in many hydrocarbon systems. This has enabled the completely synthetic field of perfluorocarbon chemistry to be developed and exploited by industry and academics with substantial financial and scholarly success.

The effects of fluorine as a substituent in organic systems have been the subject of a number of reviews,[1,5,6,7,8] those of Smart[5,6] being most insightful. This introduction will demonstrate the ways in which fluorine substitution perturbs the structure and reactivity of simple hydrocarbons.

Fluoroalkanes

The series of fluorinated methanes show an interesting trend in C-F bonding. Table 1-1[5] illustrates the strengthening and incremental shortening of the C-F bond in this series. This trend of bond strengthening with increased

Table 1-1. C-F Bond Lengths and Dissociation Energies in Fluoromethanes.

Fluoromethane	r (C-F) (Å)	D°(C-F) (kcal/mol)
CH_3F	1.385	109.0
CH_2F_2	1.358	122
CHF_3	1.332	128.0
CF_4	1.317	129.7

Table 1-2. Bond Lengths and Dissociation Energies in Fluoroethanes.

Fluoroethane	r (C-C) (Å)	D°(C-C) (kcal/mol)	D°(C-F) (kcal/mol)
CH_3-CH_3	1.532	90.4	-
CH_3-CH_2F	1.502	91.2	107.7
CH_3-CHF_2	1.498	95.6	Unknown
CH_3-CF_3	1.494	101.2	124.8
FCH_2-CF_3	1.501	94.6	109.4 (CH_2F)
CF_3-CF_3	1.545	98.7	126.8

substitution is unique to fluorine among the halogens. The series of chlorinated methanes exhibits a similar bond shortening but is accompanied by an incremental weakening; 83.7 kcal/mol down to 72.9 kcal/mol *per* first C-Cl bond homolysis in the series from CH_3Cl to CCl_4.[5]

Table 1-2[6] illustrates the effect of successive fluorination on the bond lengths and strengths in the case of ethane. Geminal fluorination leads to strengthening and shortening of the C-C bond in the series CH_3-CH_3 to CH_3-CF_3. The C-C bond lengths increase upon vicinal fluorination from CH_3-CF_3 to CF_3-CF_3 while the C-C bond strength decreases. The C-F bond strengths in the

series of ethanes follows a similar trend of strengthening with increased geminal fluorination as observed in the series of methanes.

As of this time, the trends in C-C bond strengths and lengths with various degrees of fluorination has not been fully explained. However, valence bond arguments have been used to rationalize the observed trends in C-F bonding in alkanes. As previously mentioned, fluorine contains three non-bonded electron pairs in orbitals of dimension which can accommodate appreciable overlap with orbitals of other period two elements. It is rationalized that for carbon substituted with two or more fluorines, double-bond no-bond resonance structures, or negative hyperconjugation, as shown in the classical sense by Figure 1-1, lead to increased bond order between the carbon and fluorine.[3,9,10]

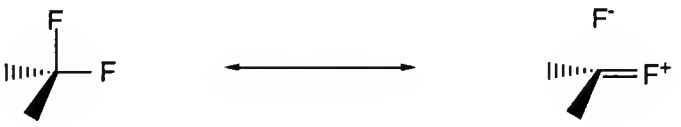


Figure 1-1. Fluorine Double-bond, No-bond Resonance.

As the degree of geminal fluorination increases, the number of valence bond structures involving doubly bound fluorine increases and the C-F bonds are increasingly shorter and stronger. Theoretical calculations at the *ab initio* level have confirmed such a bonding scheme where it is found that the stabilizing interaction arises from back-donation of a fluorine lone pair into an antibonding $\sigma^*_{C\text{-}F}$ orbital.[9,10,11] This explanation based on fluorine non-bonded electron interactions to rationalize the observed bonding and geometry characteristics in fluoro-organics is complemented by other arguments which inherently do not involve the non-bonding electrons on fluorine. One such argument suggests that when carbon is bound to more electronegative elements, atomic p character concentrates in orbitals directed towards the electronegative species

since p electrons are less tightly bound than s electrons.[12,13] Carbon rehybridization then assists in accounting for bonding and geometry trends in fluoro-organics. Another argument arising from *ab initio* level theoretical study attributes bond shortening to Coulombic interactions between oppositely charged fluorine and carbon.[14] In effect, an increase in C-F bond ionic character is predicted as the degree of fluorination increases. Calculations indicate the trend arises from negligible change in charge on fluorine but considerable increase in positive charge on carbon as the degree of fluorination increases. The variety of rationalizations for C-F bonding in such simple systems illustrates the complexities in theoretically and certainly qualitatively explaining bonding trends in fluoroorganic systems.

Fluoroalkenes

Fluorine substitution at a vinylic carbon leads to substantial changes in alkene geometry and reactivity. The data in Table 1-4[5,6] reveal that fluoroethylenes have shorter C=C bonds than ethylene and the C-F bond lengths are shorter than similarly geminal or vicinal fluorinated alkanes. The

Table 1-4. Structural Aspects of Fluoroethylenes.

	$CH_2=CH_2$	$CH_2=CHF$	$CH_2=CF_2$	$CHF=CF_2$	$CF_2=CF_2$
r(C-C) Å	1.339	1.333	1.315	1.309	1.311
r(C-F) Å	-	1.348	1.323	1.32	1.319
H-C-H deg	117.8	120.4	121.8	-	-
H-C-F deg	-	115.4	-	116.2	-
F-C-F deg	-	-	109.3	112.2	112.5
$D°_{\pi}$ kcal/mol	59.1	Unknown	62.1	Unknown	52.3

geminally difluorinated olefins contain FCF bond angles which are much smaller than ethylene and very close to the tetrahedral value of 109.47°. Theoretical *ab initio* level calculations show the C-F bond shortening can be attributed to fluorine non-bonded electron delocalization into the $\pi_{(C=C)}$ molecular orbital as depicted in a valence bond fashion by Figure 1-2.[9,15,16] FCF bond angle contraction in this case may be rationalized by attraction between the charged and neutral fluorine atoms.[16]

Figure 1-2. Fluorine Non-bonded Electron Pair Delocalization in Alkenes.

Fluoroalkene Reactivities

Reactivities in fluoroalkene series lead in some cases to clear trends as the degree of olefin fluorination is changed, but are often found to be specific to the olefin and transformation in question. Generally, reactions involving transformation of unsaturated, fluorine substituted carbon to a saturated state are more exothermic than the process for a similar hydrocarbon. Table 1-5[6] illustrates the increasing exothermicity for hydrogenations in the series of fluoroethylenes, CH_2=CHF clearly deviating from the trend. Other reactions involving saturation of CF_2=CF_2's double bond such as bromination, chlorination, HX (X = Br, Cl, I) addition, and polymerization are all in excess of 10 kcal/mol more exothermic than the corresponding reaction with ethylene.[6]

Cyclobutene to butadiene isomerizations (Table 1-6[6]) illustrate a reverse in thermal stability between the hydrocarbon (**1**) and perfluorinated (**2**) case. Perfluoro-1,3-butadiene (**2**) is found to be 11.7 kcal/mol less stable than perfluorocyclobutene, a result which is in line with the increased exothermicity

Table 1-5. Fluoroalkene Heats of Hydrogenation.

Alkene	$\Delta H°_{H_2}$ (kcal/mol)
$CH_2=CH_2$	-32.6
$CH_2=CHF$	-29.7
$CH_2=CF_2$	-38.8
$CHF=CF_2$	-45.7

Table 1-6. Fluorinated Cyclobutene/1,3-Diene Thermal Isomerizations.

	A	B	C	D	$\Delta H°$ (kcal/mol)	K_{eq} (315°C)
1	H	H	H	H	-9.7	9000
2	F	F	F	F	11.7	0.0056
3	H	H	F	F	-	77.5
4	CH_3	H	F	F	-	0.50
5	CH_2CH_3	H	F	F	-	0.24

revealed by $\Delta H°_{H_2}$ upon transcending the series of fluoroethylenes in Table 1-5. Although $\Delta H°_{H_2}$ for $CH_2=CF_2$ is 6.2 kcal/mol more exothermic than ethylene, isomerization in the case of 3,3,4,4-tetrafluorocyclobutene (**3**) favors the diene, indicating the fluoroalkene is lower in energy. Simple alkyl substitution at C1 in 3,3,4,4-tetrafluorocyclobutene as seen with **4** and **5**, dramatically shift the equilibrium towards the cyclobutene, creating doubt as to the usefulness of this system in demonstrating the thermodynamic influence of fluorine on an olefin. Other systems as illustrated in Figure 1-3,[17] indicate *gem*-difluoroolefins are

destabilized relative to the saturated species. Results pertaining to the stability of monofluorinated alkenes are contradictory but it is generally accepted that monofluorination stabilizes a double bond relative to the saturated state.[5,6]

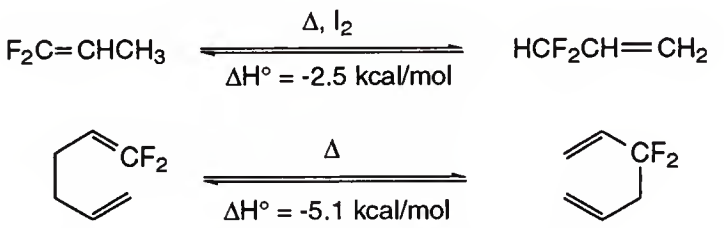


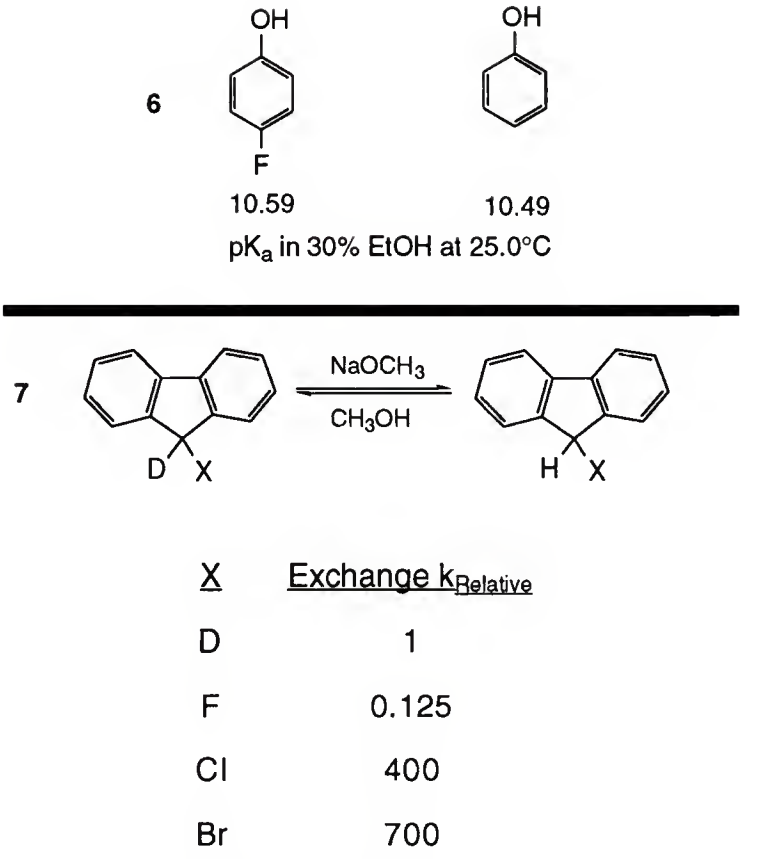
Figure 1-3. Equilibria Involving *Gem*-difluoro Alkenes.

Since the enthalpy of reaction is a relative energy change between reactant and product, it is not entirely established whether the favorable driving force for transformation of a trifluoro- of *gem*-difluoroolefin to a saturated fluoroalkane is due to π bond destabilization in the fluoroolefin or stability as a result of rehybridization of the fluorinated carbon from sp^2 in the fluoroolefin to sp^3 in the fluoroalkane. Arguments for both factors are offered and it appears that both are important in these systems with π bond destabilization being the major contributor.[5,6]

Fluorine Non-bonded Electron Interactions

As the stabilizing influence of fluorination upon alkanes has been offered, a discussion on fluorine's non-bonded electron interactions with adjacent occupied and non-occupied orbital systems is warranted in light of the aforementioned question of fluoroolefin destabilization.

Destabilization of π systems has related precedent in the case of α-fluoro carbanions. Such systems are found to be destabilized in situations where the carbon bearing the negative charge and fluorine are planar.[1] Figure 1-4



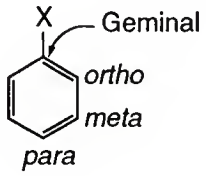
X	Exchange $k_{Relative}$
D	1
F	0.125
Cl	400
Br	700

Figure 1-4. Destabilization in Planar α-Fluorocarbanions.

illustrates the decrease in acidity in 4-fluorophenol (**6**)[18] relative to phenol and rate inhibition in isotope exchange in 9-fluorofluorene relative to fluorene-9-d_2 (**7**)[19] and other 9-halogenofluorenes. Conjugative destabilization is invoked in these cases between the fluorine non-bonded electron pairs and the planar carbanion.

A variety of experimentally observed situations occur with fluorine bound to sp^2 hybridized carbon for which perturbation of an adjacent neutral π system is induced by interaction with fluorine non-bonded electrons. Fluorine is found to be an *ortho* and *para* director and frequently a net activator in electrophillic aromatic substitutions.[7] Along the same line of thought, fluorine and oxygen are found to strongly influence the distribution of π electron charge in aromatic

Table 1-3. ^{13}C NMR Shifts (δ_{TMS}) for Heteroatom Substituted Benzene.



X	Geminal	*ortho*	*meta*	*para*
F	163.8	114.4	129.6	124.3
OH	154.9	115.4	129.7	121.0
Cl	134.3	128.6	129.8	126.5
SH	130.7	129.2	128.9	125.4

^{13}C NMR Shift for C_6H_6 [21]: 128.5

systems leading to the development of partial negative charge at the *ortho* and *para* positions. This is revealed by the observed shielding of carbons at these positions in the ^{13}C NMR spectra of representative substituted benzenes as illustrated in Table 1-3.[20] The larger third period analogies, chlorine and sulfur respectively, show a minimal effect as might be expected due to poorer overlap of their non-bonded electrons with the aromatic π system.

Direct evidence for the stabilization of carbocations by geminally substituted fluorine has been obtained by a gas phase, ion cyclotron resonance technique. This study has revealed that the ascending order of stability in the series of fluoromethyl carbocations is $^+CH_3 < {}^+CF_3 < {}^+CH_2F < {}^+CHF_2$.[22,23] Furthermore, the $^+CF_3$ cation has been generated by matrix photoionization of trifluoromethyl halides and exhibits an infrared spectrum which is consistent with extensive $\pi_{(p\text{-}p)}$ bonding.[24] Generally, the degree to which carbocations are stabilized by hydrogen, fluorine, and alkyl will be found to follow the order $^+CH < {}^+CF < {}^+CR$.[5]

α-Fluorine changes the geometry of methyl radical from planar to pyramidal which is proposed to be due to repulsion between the radical and fluorine non-bonded pairs.[25,26] Stability of α and β-fluoro radicals as established[5] from bond dissociation energies is relatively unchanged from hydrocarbon analogs and thermal rearrangement of **8** to **10** occurs with activation parameters which are almost identical when X = H or F.[27] The overall effect of fluorination on the stability of free radicals is believed to be minimal.[5,6]

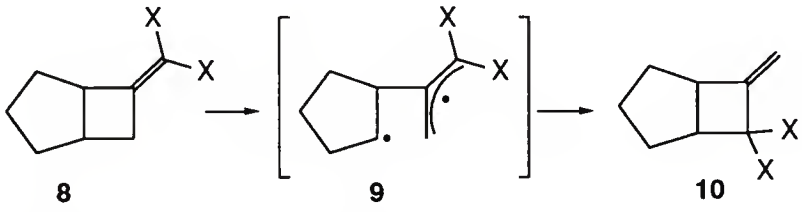


Figure 1-5. Thermal Rearrangement of 6-Methylidenebicyclo[3.2.0]heptane (**8**).

Fluorine Steric Effects

It is often assumed that when considered alone, the small differences between hydrogen and fluorine in size and bond length to carbon will lead to minimal or no effect on the conformation and reactivity in a hydrocarbon upon substitution of C-F for C-H. This is often the case and has allowed for synthesis and study of many poly and perfluorinated hydrocarbons, a situation which is not available for any other atom to the extent to which it is for fluorine. Although this is true, there remain a number of situations in which substitution of fluorine for hydrogen in a hydrocarbon leads to a profound effect on the conformation and (or) reactivity in a system due solely to the relative size and charge density of fluorine versus hydrogen.

The potential energy barrier for rotation of the C-C bond in CH_3-CH_3 is 2.8 kcal/mol whereas in CF_3-CF_3 it is increased to 3.9 kcal/mol.[28] 1,3-Repulsion

between fluorines in perfluoro-*n*-alkanes leads to a twisting in the carbon backbone. Such an effect is said to be evidenced by polytetrafluoroethylene, which below 19°C contains a 360° twist in the carbon backbone *per* 26 CF_2 units.[29] This is in marked contrast to polyethylene, where the carbon backbone maintains a *zig-zag* structure with all of the C-C bonds in the same plane and all of the hydrogen atoms in straight rows.[29] Examples of fluorine influencing conformational processes are offered in Figure 1-6.[30] In these systems, conformational barriers develop upon substitution of fluorine for hydrogen arising from electrostatic repulsion between fluorine and the group moving past. Figure 1-7 shows a persistent radical (**14**) which was able to be formed up to 88% (weight) in solution and could be diluted in the open air and dissolved in good hydrogen donor solvents like toluene, or heated to 100°C without

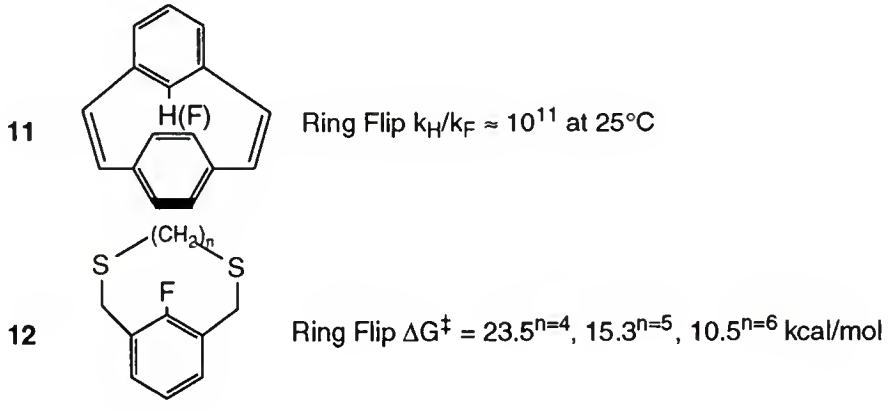


Figure 1-6. Influence of Fluorine on Conformational Processes.

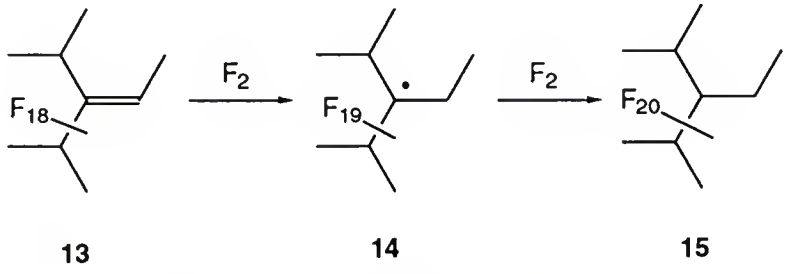


Figure 1-7. A Persistent Perfluoroalkyl Radical (**14**).

destroying the ESR signals.[1] The stability of this species was attributed to the sheltering of the radical center provided by the perfluoroethyl and perfluoroisopropyl groups. From Taft E_s values, the CF_3 group is found to be larger than $CH(CH_3)_2$ and the $CF(CF_3)_2$ group is similar in size to $C(CH_3)_3$.[31]

Steric effects attributed to fluorine are most occurrent and documented in the case of perfluorinated systems. For fluorine to exhibit a steric effect in a mono or partially fluorinated system, the molecule must exist with very small spatial tolerance, whereby substitution of hydrogen by fluorine leads to destabilization. This would be the result of attempted direct overlap of nuclei or, more likely, electrostatic repulsion between a substituent and fluorine's high negative charge density. As shown, steric effects due to fluorine are most frequently documented for conformational processes occurring in rigid systems or in the sheltering of a reaction site by a perfluoroalkyl group.

The Thermal Cyclobutene/1,3-Diene Electrocyclic Process

In the previous discussions, examples of the novelty of fluorine substituent effects were offered and rationalized based on intrinsic characteristics of the fluorine atom. With this basic groundwork in mind, the effect of fluorine on the thermal cyclobutene to 1,3-diene electrocyclic interconversion will be discussed. Understanding the studies of this system is imperative since the results lead to a hypothesis which this author's initial project (Chapter 2) was developed to further address.

An electrocyclic rearrangement is a subset of the pericyclic class of reactions which involve bonding changes in a concerted fashion through a closed cycle of atoms.[32] The electrocyclic rearrangement involves the formation of a σ bond between the termini of a conjugated linear π system which results in the formation of a ring containing one fewer π bond.[33] The reaction is potentially

reversible, a fact which will depend on the relative thermodynamics of the specific system in question.

Woodward and Hoffmann identified the thermal cyclobutene to butadiene interconversion as occurring through a concerted, conrotatory pathway.[34] Concertedness in a process, a situation where the energetics of bond breaking assist bond making,[33] is evidenced in these systems by low activation energies relative to the energy of a corresponding homolytic or heterolytic process, low activation entropies, and stereoselectivity in product formation. The stereoselectivity in the product butadiene (or cyclobutene for the reverse reaction) is a result of the conrotatory nature of this process. Woodward and Hoffmann proposed that conservation of orbital symmetry from reactants to products is the lowest energy path by which the process may occur.[34] To maintain symmetry for the thermal 4π process, C3 and C4 of cyclobutene (or terminal carbons in butadiene) must rotate in a similar direction upon breaking of the σ bond; hereby defining a conrotatory process.[34] Two equivalent, stereodistinct, conrotatory processes are allowed by orbital symmetry for the 4π thermal reaction. As shown in Figure 1-8, each leads to a different conjugated diene. Theoretical studies show that a concerted transition structure does not exist for the thermally forbidden disrotatory process and estimates the non-concerted path involving the allylmethylene diradical to be 9-11 kcal/mol above the concerted conrotatory transition state.[35]

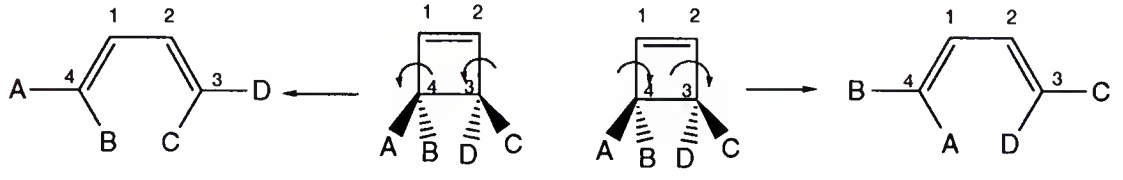
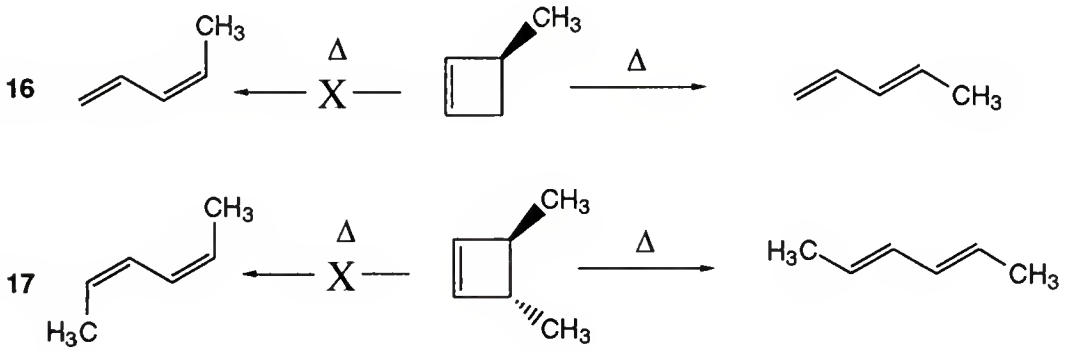


Figure 1-8. Conrotatory 4π Electrocyclic Process.

Stereochemistry of butadiene products from early thermal studies of C3 and C4 alkylated cyclobutenes were rationalized based on a steric argument. The C3 and C4 methylated cyclobutenes (Figure 1-9) yielded butadienes in which the bulkier substituent had stereospecifically rotated outward to form the



References: **16**[36], **17**[37]

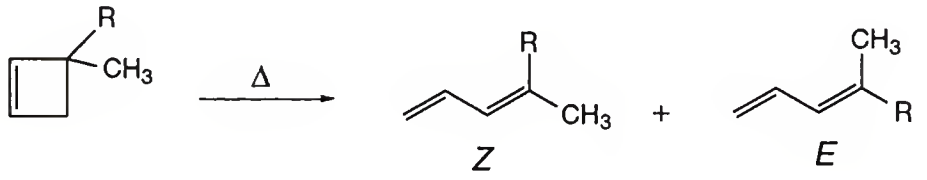
Figure 1-9. Thermal Ring Opening of Methyl Substituted Cyclobutenes.

E-alkenes, away from the breaking C3-C4 σ bond in the concerted transition state. In 1980 Curry and Stevens reported a series of 3,3-disubstituted cyclobutenes which yielded products contrary to those which would have been predicted on steric grounds.[38] Figure 1-10 illustrates their results in which ethyl, *n*-propyl, and *i*-propyl favor inward rotation over methyl to predominately form *Z*-butadienes and, surprisingly, *t*-butyl yields 32% of the product where this very bulky group has rotated inward. More intriguing examples have followed as illustrated in Figure 1-11. In each case, the reaction is 100% stereoselective and occurs contrary to expectations based on steric interactions.

Thermal Study of the Fluorinated Cyclobutene/1,3-Diene Interconversion

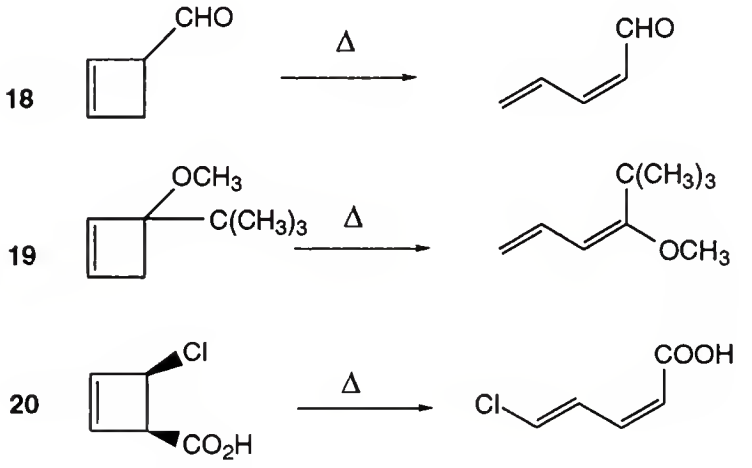
The unquantified nature of the system and an interest in fluorine substituent effects led Dolbier *et al.* to investigate the thermodynamics and

kinetics of the process for a series of fluorinated materials in the mid-1980s.[42,43] Fairly rapidly, studies in the fluorocarbon systems showed drastic deviations from the corresponding hydrocarbons. One of the major differences is that the relative thermodynamics of the perfluorocarbon systems are reversed from the hydrocarbons; at equilibrium, mainly perfluorocyclobutenes exist.[42,44] The



	Ratio of Products	
R	*Z*	*E*
Ethyl	68	32
n-Propyl	62	38
i-Propyl	66	34
t-Butyl	32	68

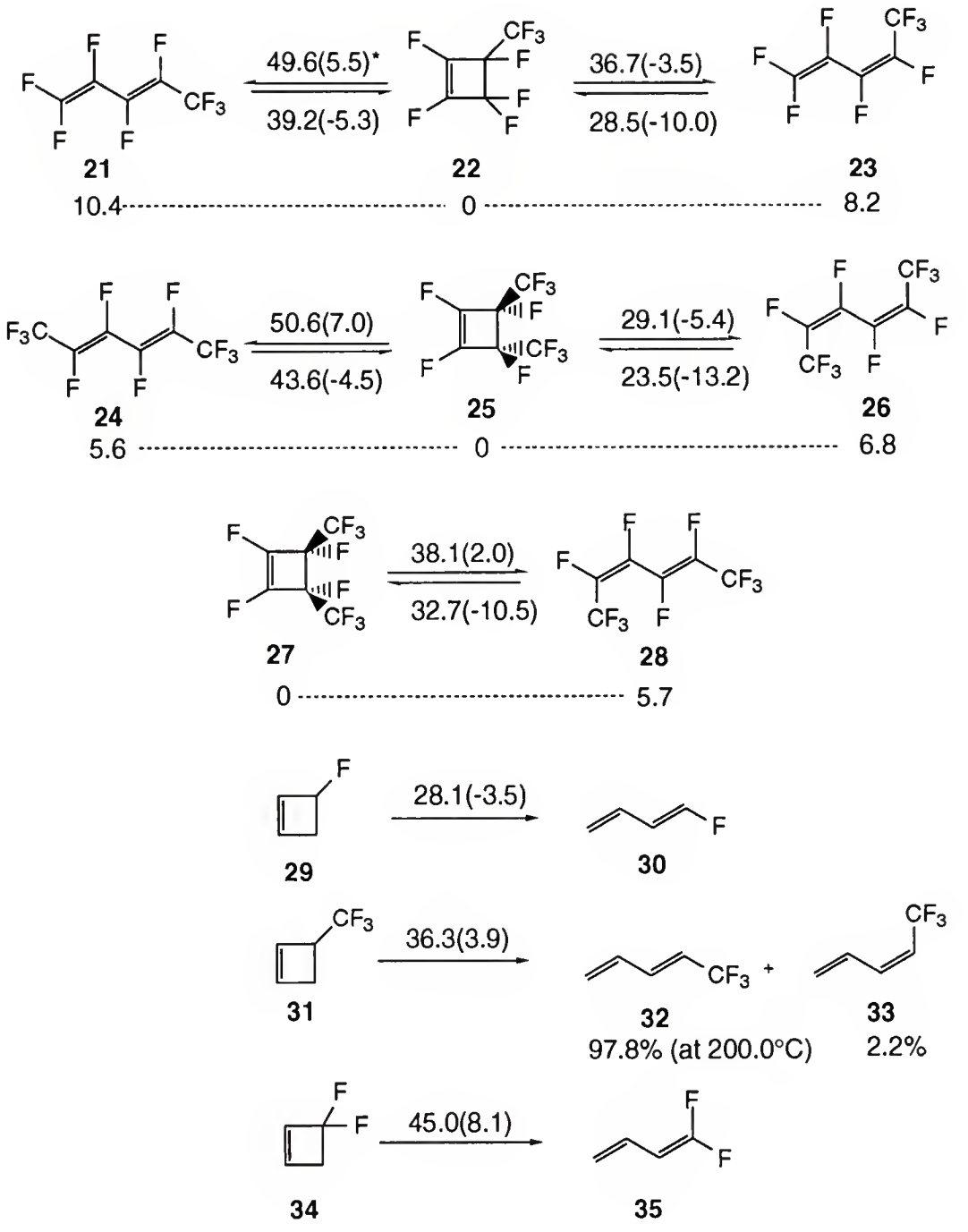
Figure 1-10. Thermal Ring Opening of 3,3-Dialkylcyclobutenes.



References: **18**[39], **19**[40], **20**[41]

Figure 1-11. Contrasteric Stereoselective Thermal Ring Openings in Substituted Cyclobutenes.

hydrocarbon cyclobutene ring opening is found to occur with $\Delta H^{\ddagger}$ = 32.0 kcal/mol,[45] $\Delta S^{\ddagger}$ = 0.1 cal/molxdeg,[45] and is irreversible at reasonable temperatures due to an exothermicity of 9.7 kcal/mol.[46] The exothermicity of the hydrocarbon process arises roughly from differences in release of cyclobutene ring strain[47] (34.0 kcal/mol) and overall bonding change of a π ($\approx$61 kcal/mol)[33] for a σ ($\approx$79 kcal/mol)[33] bond. This exothermicity is offset in the case of the perfluorinated species by the preference of fluorine to be bound to carbon orbitals hybridized with maximal p character. This factor amounts to 2 - 5 kcal/mol upon conversion of a *gem*-difluoroalkene to alkane as discussed earlier (Figure 1-3). Figure 1-12 shows some of the systems reported by Dolbier *et al.* In all of the systems, fluorine kinetically prefers outward rotation and in some cases, outward rotation of fluorine is favored even at the steric expense of rotating the bulkier CF_3 group inward. Formation of the *Z*-alkenes (**23**, **26**) from thermolysis of **22** and **25** occur with activation energies 12.9 and 27.1 kcal/mol respectively lower than the alternate processes leading to the *E*-alkenes (**21**, **24**). This corresponds to ratios of rates for *Z* and *E*-diene formation (k_Z/k_E) of 7219 and 4.3×10^6 respectively for these two systems at 200.0°C. With only one possible butadiene available from both conrotatory processes, **27** undergoes ring opening to stereospecifically yield **28** with relative normal activation parameters. The partially fluorinated cyclobutenes **29**, **31**, and **34** were investigated to quantitatively determine the effect of a single fluoro or trifluoromethyl substituent. 3-Fluorocyclobutene (**29**) was found to open stereospecifically to **30** with an activation energy 16.9 kcal/mol lower than that required for ring opening of **34**, the large difference in activation energies arising from inward rotation of a fluorine in **34** *versus* **29**. To demonstrate that thermodynamic factors were not contributing to the stereospecificities in ring opening of **29** and **31**, iodine catalyzed thermal



*Format is, E_a in kcal/mol ($\Delta S^{\ddagger}$, cal/molxdeg); Relative $\Delta H°$ in kcal/mol is shown below structures for **21-23**, **24-26**, **27-28**. References: (**21-28**)[42], (**29-35**)[43]

Figure 1-12. Thermal Fluorocyclobutene/Fluoro-1,3-Diene Interconversions Studied by Dolbier *et al.*

equilibria of each butadiene system was examined. *Z*-1-Fluoro-1,3-butadiene was found to be more stable than the *E*-diene **30** with $K_{(Z/E)}$ of 1.77 at 60 °C and *E*-5,5,5-trifluoro-1,3-pentadiene (**32**) was more stable than *Z*-**33** with $\Delta H° = 2.5$ kcal/mol for the $E \leftrightarrow Z$ equilibrium. No significant thermodynamic difference between the *Z* and *E*-alkenes was observed in any of the cases examined, as evidenced by these small differences in $\Delta H°$ values. Therefore in these systems, the observed kinetic difference must derive from substituent effects on the relative transition state stability for the two competing conrotatory processes. Considering all of the data, it was determined that in thermal conrotatory cyclobutene ring openings, inward rotation of fluorine raises the activation energy for the process by 10 kcal/mol while outward rotation lowers it by 4 kcal/mol.[43]

Theoretical Study of the Thermal Cyclobutene/1,3-Diene Interconversion

From the variety of examples and the nature of substituents examined for this 4π, thermal process, it was obvious that the stereoselectivities observed were not steric in origin except in a minor number of cases. Rather, the stereoselectivities originate from a strong electronic effect involving interaction of cyclobutene C3 and C4 position substituents with molecular orbitals of the 4π transition state. Substituents at the C3 and C4 positions able to act as π electron donors such as F, Cl, OCH_3, and $OCOCH_3$, kinetically favored outward rotation whereas π electron acceptors such as CHO and COOH favored inward rotation.

Rondan and Houk developed a hypothesis around results obtained by theoretical *ab initio* level calculations on the cyclobutene/1,3-diene thermal conrotatory process.[48] Figure 1-13 is a representation of their proposed HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied

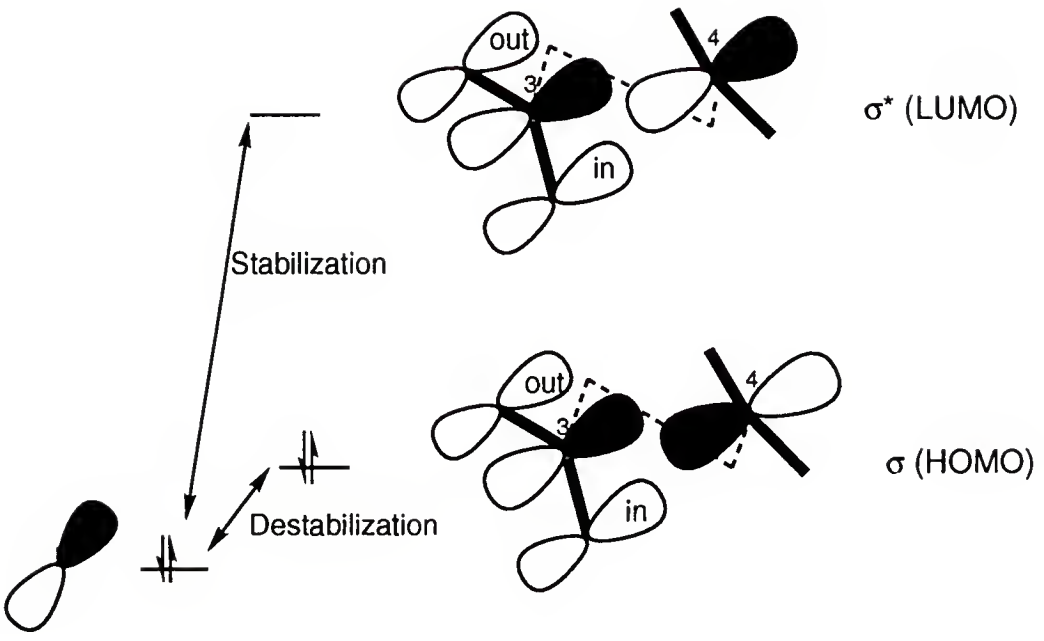


Figure 1-13. Representation of Donor Orbital Interactions with the HOMO and LUMO of the Cyclobutene Conrotatory Transition Structure.

Molecular Orbital) for the cyclobutene thermal electrocyclic, conrotatory ring opening transition structure with the donor orbital system indicated for either outward or inward rotation. Upon inward rotation, a donor orbital (π_{CH_3} on CH_3 or a lone pair of electrons on a heteroatom) destabilizes the transition state due to a repulsive interaction with the occupied bonding σ orbital, while minimal interaction exists with σ^* as the donor orbital is directed at the nodal surface. Outward rotation of a donor is slightly stabilizing due to overlap with the σ^* and the fact that the donor orbital experiences less repulsion with σ upon rotating out. Interaction of acceptors containing a π bond is more complicated due to the interactions of occupied π bonding and unoccupied π^* antibonding orbitals with the σ and σ^* orbitals of the cyclobutene transition state. The maximal stabilizing interaction in the case of acceptors containing a π bond is proposed to occur upon inward rotation. The two electron interaction between the cyclobutene

C3-C4 σ orbital and the π^* orbital on the acceptor leads to a small preference for inward rotation. Experimentally, acceptors show little preference for inward or outward rotation, the reason being that the stabilizing π^*-σ interaction is countered by a repulsive interaction between the occupied π orbital and C3-C4 σ orbital of the cyclobutene transition structure. Rondan and Houk suggested a powerful electron acceptor such as the empty p orbital on a BH_2 group would favor inward rotation due to the strong interaction with the occupied cyclobutene σ bonding orbital. Table 1-7[48] illustrates calculated ΔE_a's for inward *versus* outward rotation for BH_2 and other donor and acceptor substituents which further demonstrate strong rotational selectivities.

Table 1-7. Calculated ΔE_a's for Inward versus Outward Rotation in Substituted Cyclobutenes.

Substituents	$E_a^{out} - E_a^{in}$
trans-3,4-diboryl	+13
trans-3,4-dimethyl	-13
trans-3,4-dichloro	-22
trans -3,4-difluoro	-29
trans-3,4-dihydroxy	-31.6

The cleavage of the σ bond in the cyclobutene system biased by the electronic character of an attached substituent was dubbed "torquoselectivity" by Houk.[49] He argues that in this system, the torque about the stretching σ bond is controlled by interaction with geminal electron donor or acceptor substituents. It is further stated that such electronic based selectivities should be observable in a variety of other organic pericyclic processes.

Conclusion

The preceding discussions have introduced the variety and fashion in which fluorine substitution can perturb hydrocarbon chemistry and aid in mechanistic interpretation. The body of this thesis will address experimental results obtained from the study of fluorine as a substituent in thermal and photochemical 6π electrocyclic (Chapter 2) and thermal [3,3]-sigmatropic rearrangements (Chapter 3).

CHAPTER 2

THERMAL AND PHOTOCHEMICAL REARRANGEMENTS OF 9,10-BIS(TRIFLUOROETHENYL)PHENANTHRENE AND PERFLUORO-*E,E,E*- AND *E,Z,E*-4,5-DIMETHYL-2,4,6-OCTATRIENE

Introduction

The concept of torquoselectivity, developed by Rondan and Houk to rationalize the strong electronic control of C3 and C4 substituents upon ring opening of cyclobutenes, was suggested to be operating in a variety of pericyclic processes. The potential was discussed for various processes such as 6π electrocyclic reactions, cyclopropane isomerizations, and sigmatropic shifts, to undergo σ bond cleavage in a stereoselective fashion biased by overlap with geminally bound acceptor or donor substituents.[48,49] Disrotatory electrocyclic processes are expected to exhibit rotational preferences to a smaller degree than those observed for conrotatory cases. This is due to a smaller difference in overlap (Figure 2-1) between the breaking σ bond and geminal substituent in inward and outward rotational configurations for disrotatory as compared to conrotatory processes.

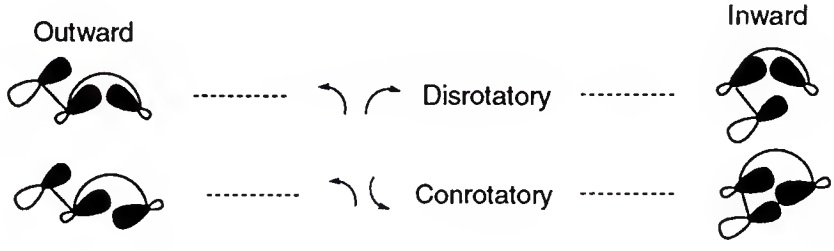


Figure 2-1. Geminal Substituent Overlap With σ Bond in Outward and Inward Rotation for Disrotatory and Conrotatory Processes.

Surprisingly, probing of torquoelectronic effects through suitably designed systems has received minimal attention outside of the thermal cyclobutene ring opening examples discussed in Chapter 1. Torquoselectivity in the electrocyclic conversion of benzocyclobutenes to *o*-xylylenes has been studied through Diels-Alder trapping experiments.[50] A few examples involving cyclopropane ring cleavage, such as: solvolysis of cyclopropyl halides,[51] 1,3-sigmatropic shifts of substituted methylenecyclopropanes,[49] and retro-ene reactions of methyl vinylcyclopropanes,[49] have been rationalized assisted by torquoelectronic arguments.

In light of the torquoelectronic effects observed in the thermal 4π electrocyclic fluorinated cyclobutene/1,3-diene system and the relatively unexplored question of applicability to other pericyclic processes, a study of the thermal 6π electrocyclic fluorinated 1,3(*Z*),5-triene/1,3-cyclohexadiene interconversion was proposed. Woodward and Hoffman described the thermal 6π 1,3(*Z*),5-triene to 1,3-cyclohexadiene reaction as occurring through an orbital symmetry allowed disrotatory pathway.[34] Experimentally, it is found that the cyclized products are formed in a stereospecific fashion in line with a disrotatory closure involving rotation of terminal 1,3(*Z*),5-triene substituents in an opposite sense as illustrated by the examples in Figure 2-2.[52]

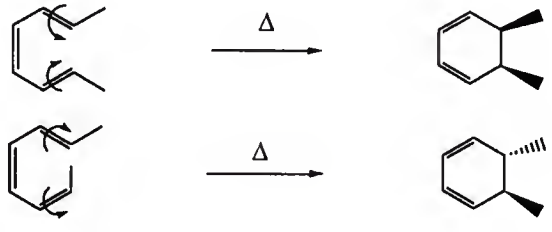


Figure 2-2. Stereospecific Thermal Disrotatory 6π Electrocyclizations.

For hydrocarbon 1,3(*Z*),5-trienes, a wide variety of substituted systems have been investigated to establish the relationship between triene structure and reactivity towards cyclization.[53]

Observing torqueoelectronics in thermal ring opening of this 6π system is unlikely, as the thermodynamics for conversion of 1,3-cyclohexadiene (**38**) to *Z*-1,3,5-hexatriene (**37**) are unfavorable. The enthalpy diagram in Figure 2-3[54] illustrates the conversion of **37** to **38** is 15 kcal/mol exothermic due to loss of

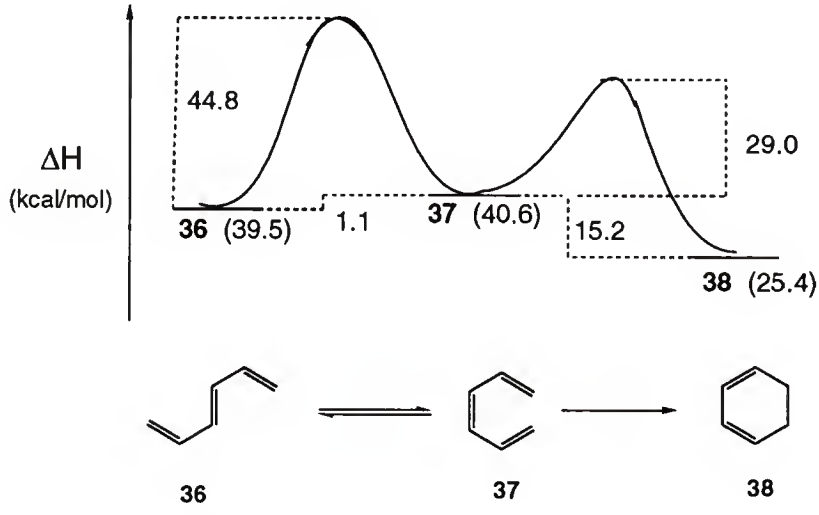


Figure 2-3. Enthalpy Diagram for *E* and *Z*-1,3,5-Hexatriene (**36**, **37**) and 1,3-Cyclohexadiene (**38**).

the conjugated triene double bond and formation of a σ bond in 1,3-cyclohexadiene. 1,3(*Z*),5-Triene *Z*→*E* isomerization (**37**→**36**) does not compete with 6π cyclization at lower temperatures as such a process involves homolytic cleavage of the central double bond, occurring with a transition state 16 kcal/mol higher in energy than that required for the electrocyclic process. The large exothermicity observed for *Z*-1,3,5-hexatriene cyclization leads to an estimated $\Delta H^{\ddagger}$ = 44 kcal/mol for ring opening of 1,3-cyclohexadiene. This magnitude of an energy barrier for ring opening also accommodates a variety of

sigmatropic shift processes. Retrocyclizations of substituted 1,3-cyclohexadienes have been observed at higher temperatures but stereochemical analysis of the formed 1,3(*Z*),5-trienes in search of torquoelectronic effects is futile due to competing rearrangements. Ring opening of **39** (Figure 2-4) at 560°C led to complete equilibration of the labels and was rationalized as occurring through retrocyclizations and [1,7]-H(D)

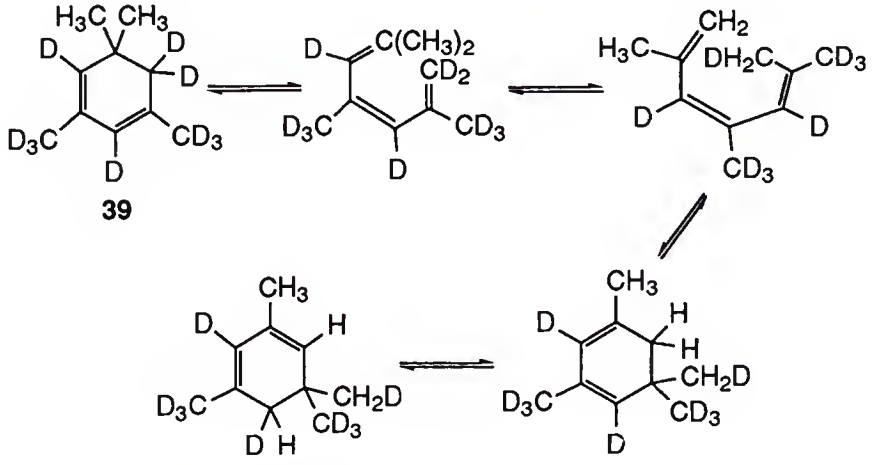


Figure 2-4. Thermal Ring Opening of a 1,3-Cyclohexadiene.

shifts.[55] 1,3,5-Triene *Z*↔*E* isomerizations will also be competitive at these elevated temperatures and create another source of stereochemical scrambling.[56,57]

It is obvious from the preceding discussion that productive ring opening and observation of torquoelectronics in substituted 1,3-cyclohexadienes will require an adjustment in the thermodynamics of this system. In effect, reduction or reversal of the enthalpy difference between a 1,3(*Z*),5-triene and 1,3-cyclohexadiene would allow retrocyclization to be observed. The achievement of such a situation would allow for ring opening of a 1,3-cyclohexadiene system to occur at a reasonable temperature and allow study of torquoelectronic effects

by observing the 1,3(*Z*),5-triene stereochemistry and activation parameters required.

Development of a Suitable 1,3(*Z*),5-Triene/1,3-Cyclohexadiene System

In theory, the exothermicity of 1,3(*Z*),5-triene cyclization may be offset by ground state stabilization of the 1,3(*Z*),5-triene, destabilization of the 1,3-cyclohexadiene, or some combination of both.

A system in which the thermodynamics seem favorable for observing ring opening of a 1,3-cyclohexadiene is one in which the 1,3(*Z*),5-triene/1,3-cyclohexadiene system shares a π bond with an aromatic ring as illustrated for a general case in Figure 2-5. Cyclization in this case is impeded by loss of the aromatic ring π bond, in effect destroying the resonance energy for that ring in the aromatic system. By selecting the appropriate aromatic system and

Figure 2-5. Aromatic Annulated 1,3(*Z*),5-Triene/1,3-Cyclohexadiene System.

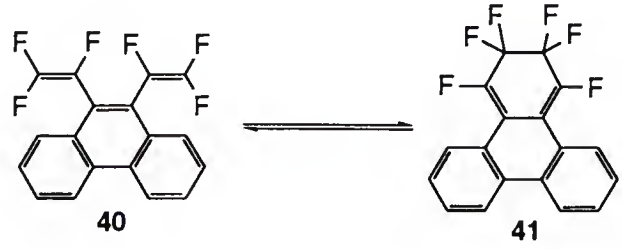
placement, 1,3-cyclohexadiene ring opening can become a competitive process with 1,3(*Z*),5-triene cyclization at lower temperatures. Building a fluorinated 1,3(*Z*),5-triene system into an phenanthrene ring was believed to be the best suited entry into thermal study of 1,3-cyclohexadiene ring opening.

As previously discussed, *Z*-1,3,5-hexatriene cyclization is exothermic by 15 kcal/mol and terminal *gem*-difluorination or trifluorination of an pendant alkene will increase this value by 2-5 kcal/mol *per* alkene. In line with the C-C σ bond strengthening trend observed for the series of fluorinated ethanes (Chapter 1, Table 1-2), the C5-C6 σ bond in the cyclohexadiene product will be

stronger than the corresponding C5-C6 σ bond in the hydrocarbon. Such an effect is difficult to quantitize due to the nonlinear energy changes in geminal bond strengths upon successive fluorination. An increase in the exothermicity of the cyclization process from formation of the tetrafluorinated C5-C6 σ bond can be estimated to have an upper limit of 8 kcal/mol obtained from the difference in C-C σ bond strength between CH_3-CH_3 and CF_3-CF_3 (Chapter One, Table 1-2). This yields an potential enthalpy of reaction range of -19 kcal/mol to -33 kcal/mol for cyclization of the hypothetical 1,1,2,5,6,6-hexafluoro-1,3(*Z*),5-hexatriene. Although conceptually straightforward, estimation of this $\Delta H°_R$ using $\Delta H°_F$ of each species through Benson[58] type group values cannot be performed because of the missing groups; CD-(CD)(F), CD-(C)(F), and C-(C)(CD)(F)(F).[59] Likewise, theoretical computations at any level less than *ab initio* lead to woefully incorrect energy parameters for fluorinated materials.[60]

The resonance energy for phenanthrene is observed to be 91 kcal/mol.[61] Loss of phenanthrene's C9-C10 double bond is accompanied by an 20 kcal/mol increase in enthalpy, or the difference in resonance energy between phenanthrene and biphenyl.[61,62]

Considering the energetics of the 1,3(*Z*),5-fluorotriene cyclization and disruption of phenanthrene resonance energy by C9-C10 π bond cleavage



40 **41**

Figure 2-6. Proposed Thermal Electrocyclic Interconversion between 9,10-Bis(trifluoroethenyl)phenanthrene (**40**) and 1,2,2,3,3,4-Hexafluoro-2,3-dihydro-triphenylene (**41**).

together in a single system such as 9,10-bis(trifluoroethenyl)phenanthrene (**40**) and 1,2,2,3,3,4-hexafluoro-2,3-dihydrotriphenylene (**41**) as illustrated in Figure 2-6, an enthalpy of reaction range of 1 kcal/mol to -13 kcal/mol for the cyclization may be predicted based on the previous arguments. The upper limit of such an enthalpy difference is suitable to allow for potential study of forward and reverse reactions under reasonable conditions and, ultimately, observation of torquoelectronic effects in a higher substituted system such as illustrated in Figure 2-7. Due to a straightforward synthetic route available into these perfluoroalkenyl substituted aromatics, **40** was prepared for thermal study.

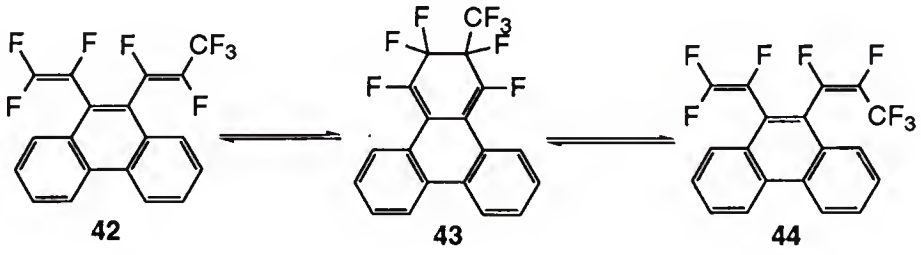


Figure 2-7. Unsymmetrically Substituted, Phenanthrene Annulated, 1,3(*Z*),5-Triene/1,3-Cyclohexadiene Interconversion for Torquoelectronic Study.

Synthesis of 9,10-Bis(trifluoroethenyl)phenanthrene (**40**)

9,10-Bis(trifluoroethenyl)phenanthrene (**40**) was synthesized in four steps (Figure 2-8) and isolated in a 1% overall yield. The first two steps involved literature procedures; bromination[63] of phenanthrene (**45**) to yield 9-bromophenanthrene (**46**, 90%), then nitration[64] to yield 9-bromo-10-nitrophenanthrene (**47**, 13%). The actual yield of **47** from this reaction was higher. The isolated yield reflects some difficulty in obtaining this material pure from the other major nitration product, 9-bromo-3-nitrophenanthrene. The next step involved nucleophillic attack of iodide on the brominated C9 of **47** to yield

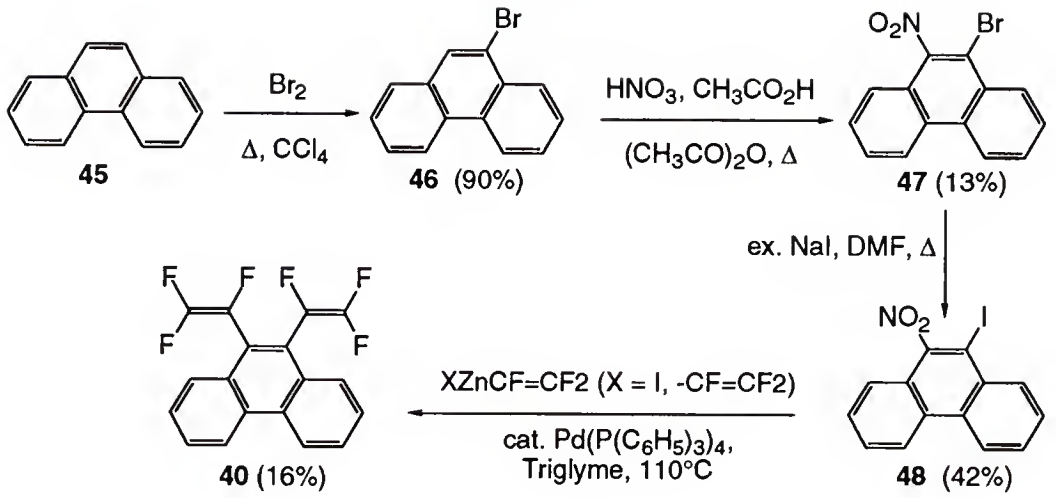


Figure 2-8. Synthesis of 9,10-Bis(trifluoroethenyl)phenanthrene (**40**).

9-iodo-10-nitrophenanthrene (**48**, 42%). The best literature procedure found for preparation of **48** involved five steps and produced the target in 1% yield from phenanthrene.[65] Our procedure is a significant improvement even in this unoptimized state involving three steps and producing **48** in 5% isolated yield from phenanthrene. Preparation of **40** at this point was rather fortuitous. A $Pd(P(C_6H_5)_3)_4$ catalyzed coupling between iodo aryls and XZnCF=CFY (X = I or -CF=CFY, Y = F or *Z*(*E*)-CF_3) was carried out on **48**.[66] From the reaction mixture, 16% of **40** could be isolated on average. It was intended to isolate 9-nitro-10-trifluoroethenylphenanthrene by this procedure, which through subsequent steps could be converted to 9-iodo-10-trifluoroethenyl-phenanthrene. This material would then provide the desired **40**, **42**, and **44** through the appropriate coupling procedure. Preparation of **40** by this coupling procedure with **48** was found to be reproducible over a number of runs. Although 9-nitro-10-trifluoroethenylphenanthrene was tentatively identified as a component in the reaction mixture by ^{19}F NMR, it was never isolated. Having

40 in hand a few steps earlier than anticipated, a study of it's thermal chemistry was initiated.

Thermal Study of 9,10-Bis(trifluoroethenyl)phenanthrene (**40**)

The thermolysis **40** was studied from 140°C up to 193°C as 0.1 M solutions in C_6D_6. Upon thermolysis of **40**, four products could be observed in solution and were isolated pure by preparative GLPC for characterization. Figure 2-9 illustrates the percent composition of all reaction components *versus* time for thermolysis at 180.0°C. The reaction is quantitative with regard to formation of $C_{18}H_8F_6$ structural isomers through 19 hours of thermolysis at 180.0°C and after 235 hours, a 78% yield of $C_{18}H_8F_6$ isomers is obtained as a 21:1 mixture of 1,2-(9,10-phenanthro)-3,5,5-trifluoro-4-trifluoromethyl-1,3-cyclopentadiene (**51**) and 1,2,2,3,3,4-hexafluoro-2,3-dihydrotriphenylene (**41**).

To develop the scheme of overall transformations as shown in Figure 2-9, it was necessary to thermolyze each of the intermediate materials; **41**, 1,4,4,5,6,6-hexafluoro-2,3-(9,10-phenanthro)-bicyclo[3.1.0]hex-2-ene (**49**), and 4-difluoromethylidene-3,3,5,5-tetrafluoro-1,2-(9,10-phenanthro)cyclopent-1-ene (**50**), alone under conditions which had been used for the parent triene **40**. Thermolysis of **41** at 180.0°C as a 6:1 purified mixture of **41**:**51** led to non-productive decomposition of **41** with no reaction of **51**. Triene **40** was not observed to be reversibly formed from the cyclized product **41**, and neither **49** nor **50** were observed either. Thermolysis of purified **49** was observed at three temperatures (180°C, 185.0°C, 192.5°C) and found to form only **50** and **51**. The conversion of **49** to **50** and **51** is quantitative at the temperatures and times observed. Figure 2-10 illustrates the percent composition of all reaction components *versus* time for thermolysis of **49** at 180.0°C. Thermolysis of **50**, as one can see at longer times in thermolysis of **40** (Figure 2-9, after 140 hours)

is observed to slowly form **51** in a near quantitative process. The possibility of fluoride catalysis affording such a rearrangement was demonstrated by the rapid conversion of **50** to **51** at 80°C in the presence of added trace amounts of CsF.

The possibility of fluoride catalysis effecting the reaction course of **40** at early times was ruled out by thermolyzing a sample of **40** in DMF containing CsF at 115°C. After 3.5 hours, 70% of **40** had been consumed and three other products were observed. Analysis of this mixture by GLPC and ^{19}F NMR showed that this fluoride catalyzed reaction process and the thermal process had no products in common and was not further investigated.

The disappearance of **40** and **49** were both found to follow first-order kinetics, and the corresponding first-order plots are given in Figure 2-11 and Figure 2-12 respectively. Upon thermolysis of **40** up to 85% conversion, the ratio of (**49**+**50**+**51**)/**41** was maintained at 4.42 ± 0.19 at 180.0°C, 5.03 ± 0.11 at 184.5°C, and 5.15 ± 0.16 at 193.0°C. Upon thermolysis of **49** through 70% conversion, the ratio of (**50**/**51**) was maintained at 1.62 ± 0.12 at the three temperatures (180.0°C, 185.0°C, 192.5°C) examined. As previously mentioned, the reactions of **40** and **49** were found to be irreversible in formation of their respective products. Assuming these reactions occurred *via* irreversible, competitive first-order processes, rate constants for formation of **41** and **49** from **40**, and **50** and **51** from **49** were obtained from the observed rate constants for loss of **40** and **49**, and the constant ratios of respective products formed.[67] Both the observed and separated rate constants for **40** are reported in Figure 2-11, and for **49** in Figure 2-12.

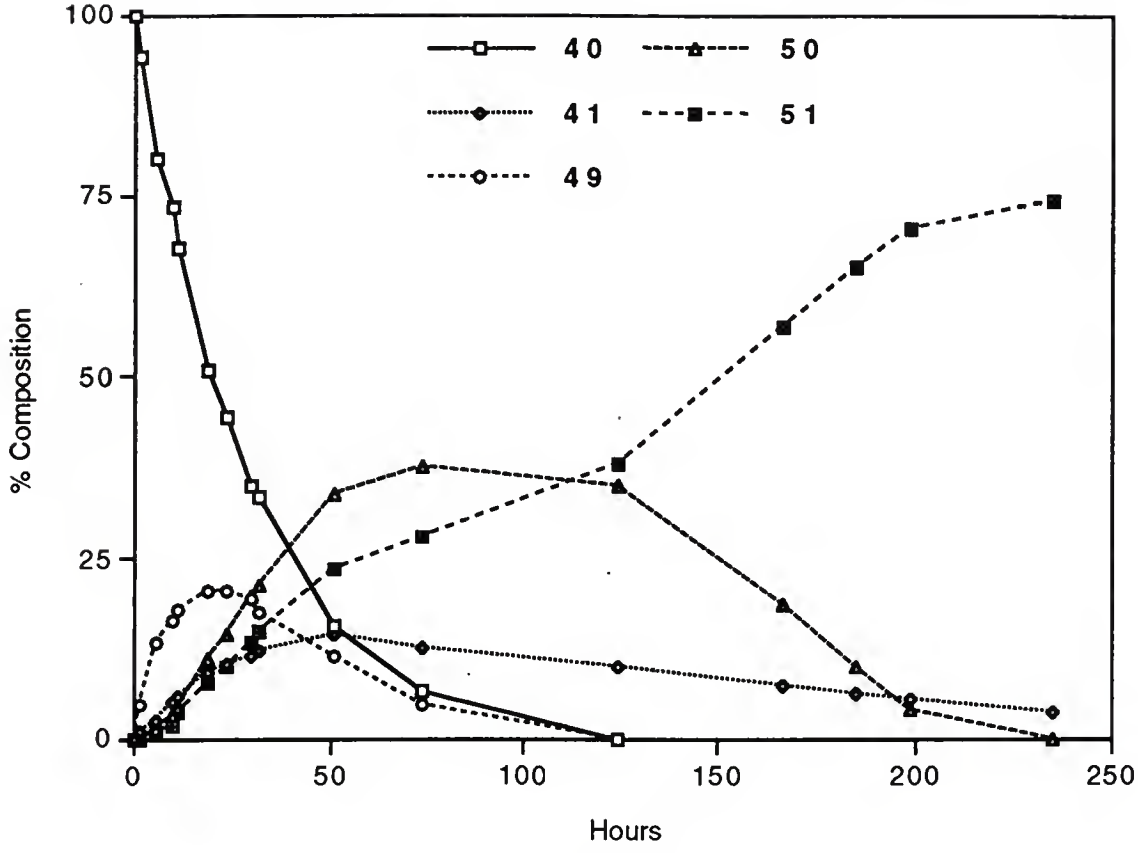
The activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$) for the individual processes were obtained from the Eyring expression[68], $k = \frac{kT}{h} e^{\left(-\frac{\Delta H^{\ddagger}}{RT}\right)} e^{\left(\frac{\Delta S^{\ddagger}}{R}\right)}$, rearranged to the

form Ln(k/T) = $-\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R + Ln(k/h)$, where k = rate constant at absolute temperature T, ***k*** = Boltzmann constant (1.381×10^{-23} J/K), ***h*** = Planck's constant (6.626×10^{-34} Jxs), and R = ideal gas constant (1.9872 cal/molxK). Linear least-squares regression plots of Ln(k/T)*versus* 1/T yielded $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ from the slope and intercept respectively of the fitted line for each system. Fit of the separated rate constant k_{41} (Figure 2-13) at the three observed temperatures yielded $\Delta H^{\ddagger}$ = 29.9 ± 0.1 kcal/mol and $\Delta S^{\ddagger}$ = -19.6 ± 0.3 cal/molxdeg, and for k_{49} (Figure 2-13) yielded $\Delta H^{\ddagger}$ = 34.4 ± 2.8 kcal/mol and $\Delta S^{\ddagger}$ = -6.6 ± 6.0 cal/molxdeg. Fit of the separated rate constant k_{50} (Figure 2-14) yielded $\Delta H^{\ddagger}$ = 31.3 ± 0.4 kcal/mol and $\Delta S^{\ddagger}$ = -12.7 ± 0.9 cal/molxdeg, and for k_{51} (Figure 2-14) yielded $\Delta H^{\ddagger}$ = 31.4 ± 0.1 kcal/mol and $\Delta S^{\ddagger}$ = -13.4 ± 0.1 cal/molxdeg.

Quantitative thermal studies of fluorinated 1,3,5-trienes have no precedent in the literature, and the formation of bicyclo[3.1.0]hex-2-ene ring structures from 1,3,5-triene thermolyses have no precedent in fluorocarbon literature. There has been but one such case observed in the hydrocarbon literature, and this will be discussed later. The novelty of the chemistry presented above, along with the general absence of thermal studies of fluorinated 1,3,5-trienes, led to examination of the system which will be discussed next.

Thermal Study of an Acyclic Perfluorinated 1,3,5-Triene

The unexpected thermal results obtained in the case of **40** led to our questioning as to whether an acyclic perfluorinated 1,3(*Z*),5-triene would also undergo bicyclo[3.1.0]hex-2-ene ring formation in preference to the thermal disrotatory 6π electrocyclic process. At the time this project began, the literature contained only one relevant reference. Perfluoro-1,3,5-hexatriene had been reported to afford an 84% yield of perfluoro-1,3-cyclohexadiene upon pyrolysis



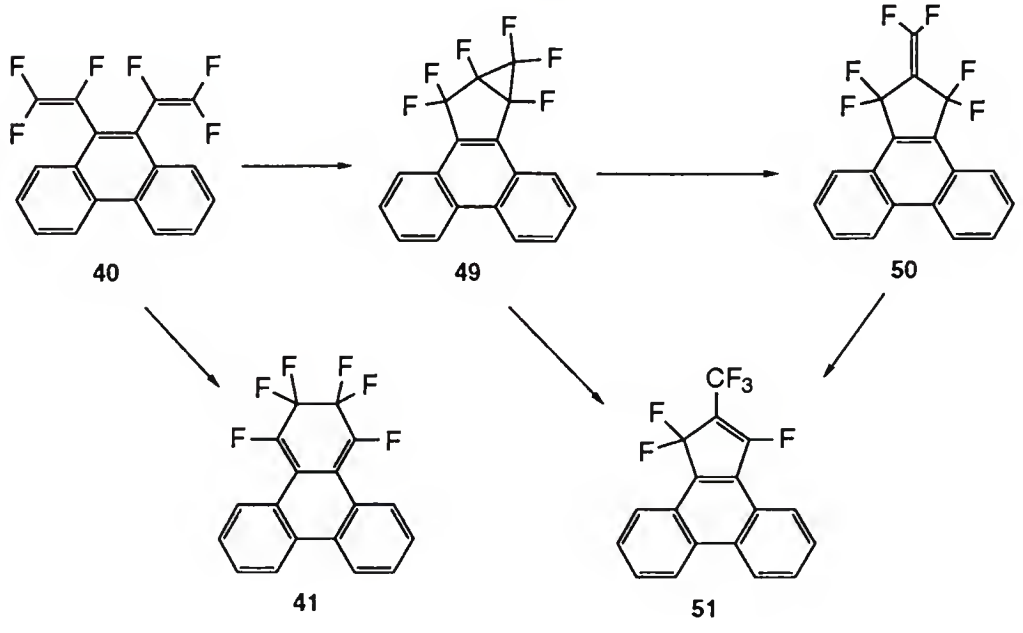


Figure 2-9. Thermolysis of 9,10-Bis(trifluoroethenyl)phenanthrene (**40**) at 180.0°C as a Solution in C_6D_6.

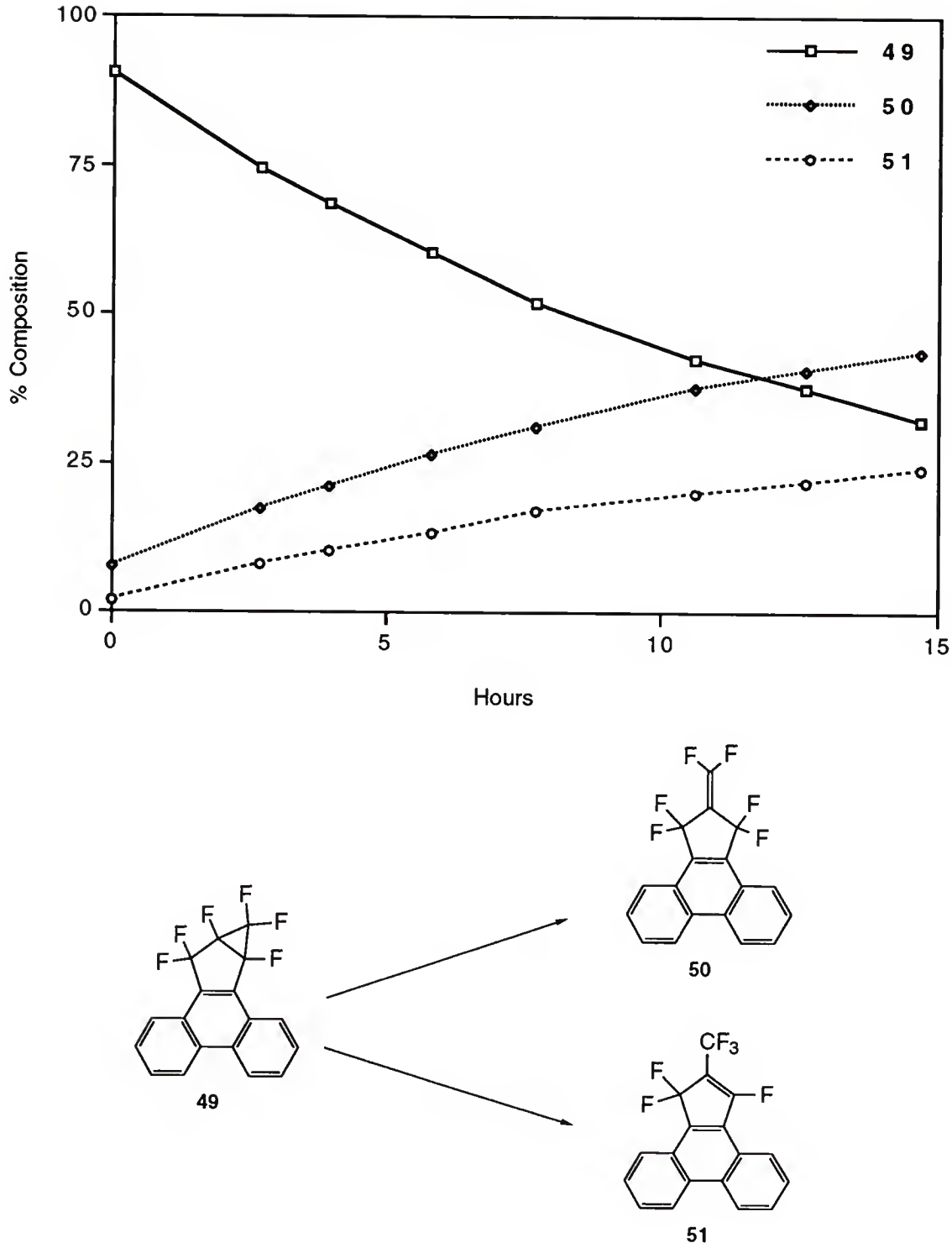
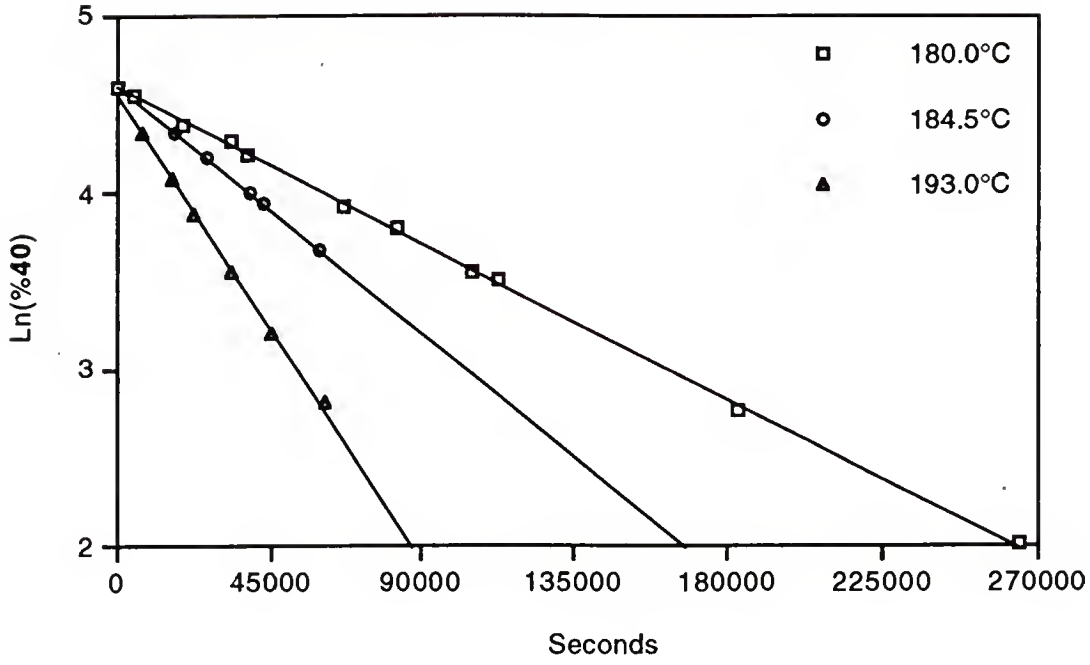


Figure 2-10. Thermolysis of 1,4,4,5,6,6-Hexafluoro-2,3-(9,10-phenanthro)-bicyclo[3.1.0]hex-2-ene (**49**) at 180.0°C as a Solution in C_6D_6.



T (°C)	k_{40} ($\times 10^5$ sec^{-1})	k_{41} ($\times 10^5$ sec^{-1})	k_{49} ($\times 10^5$ sec^{-1})
180.0	0.991 ± 0.12	0.183	0.808
184.5	1.55 ± 0.01	0.257	1.29
193.0	2.93 ± 0.06	0.476	2.45

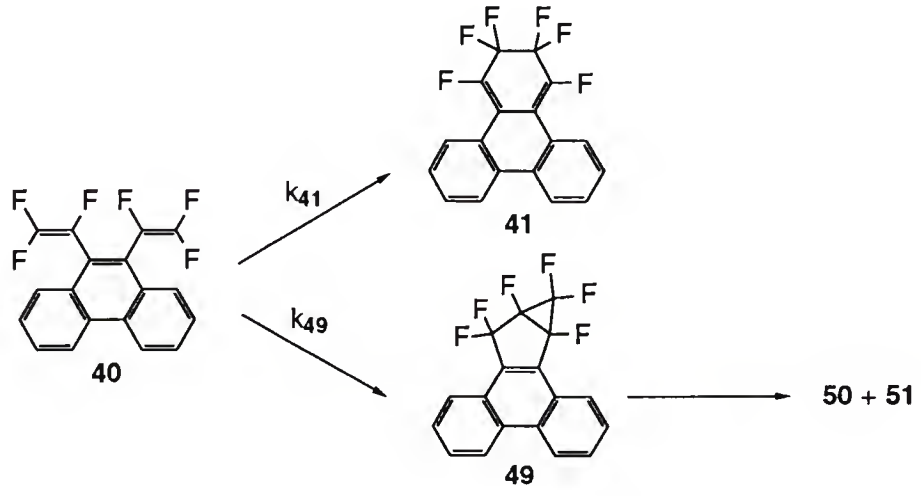
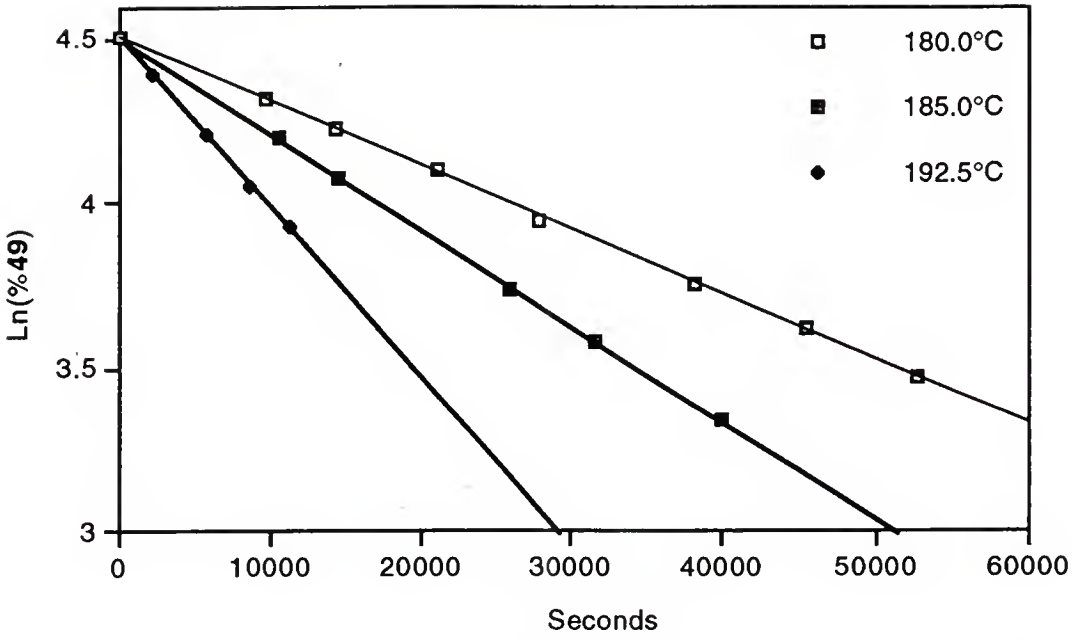


Figure 2-11. First-Order Plots and Rate Constants for Loss of 9,10-Bis(trifluoroethenyl)phenanthrene (**40**) and Derived First-Order Rate Constants for Formation of 1,2,2,3,3,4-Hexafluoro-2,3-dihydrotriphenylene (**41**) and 1,4,4,5,6,6-Hexafluoro-2,3-(9,10-phenanthro)bicyclo[3.1.0]hex-2-ene (**49**).



T (°C)	k_{49}(x10^5 sec^{-1})	k_{50}(x10^5 sec^{-1})	k_{51}(x10^5 sec^{-1})
180.0	1.96 ± 0.02	1.21	0.751
185.0	2.92 ± 0.01	1.81	1.11
192.5	5.14 ± 0.08	3.17	1.97

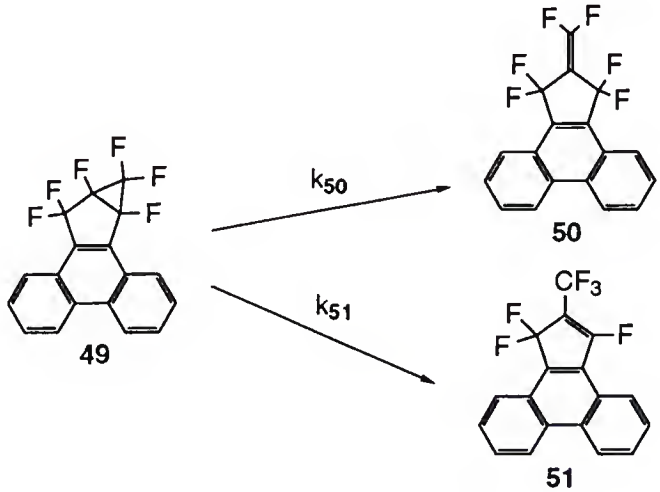


Figure 2-12. First-Order Plots and Rate Constants for Loss of 1,4,4,5,6,6-Hexafluoro-2,3-(9,10-phenanthro)bicyclo[3.1.0]hex-2-ene (**49**) and Derived First-Order Rate Constants for Formation of 4-Difluoromethylidene-3,3,5,5-tetrafluoro-1,2-(9,10-phenanthro)cyclopent-1-ene (**50**) and 1,2-(9,10-Phenanthro)-3,5,5-trifluoro-4-trifluoromethyl-1,3-cyclopentadiene (**51**).

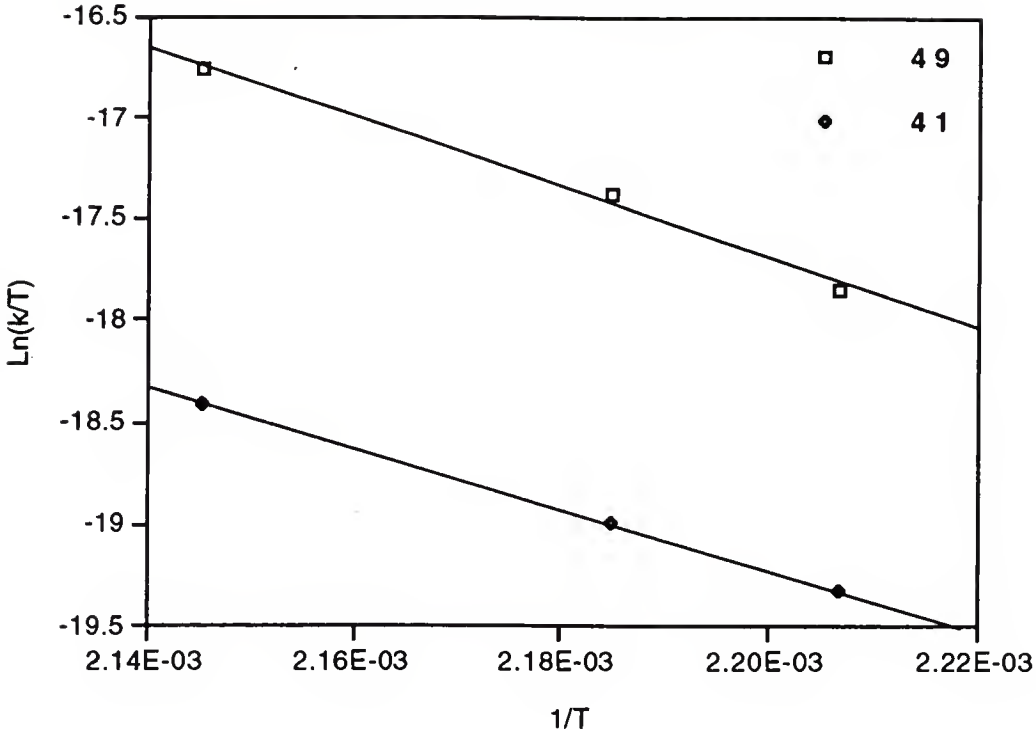


Figure 2-13. Eyring Plots for Separated Rate Constants k_{41} and k_{49}.

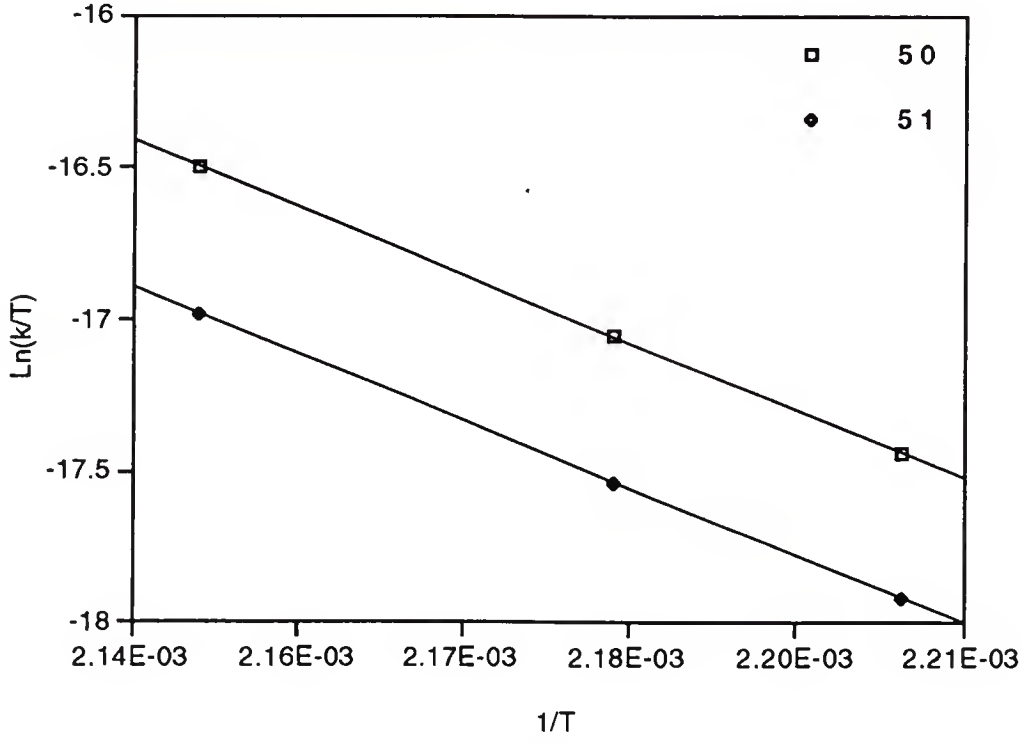
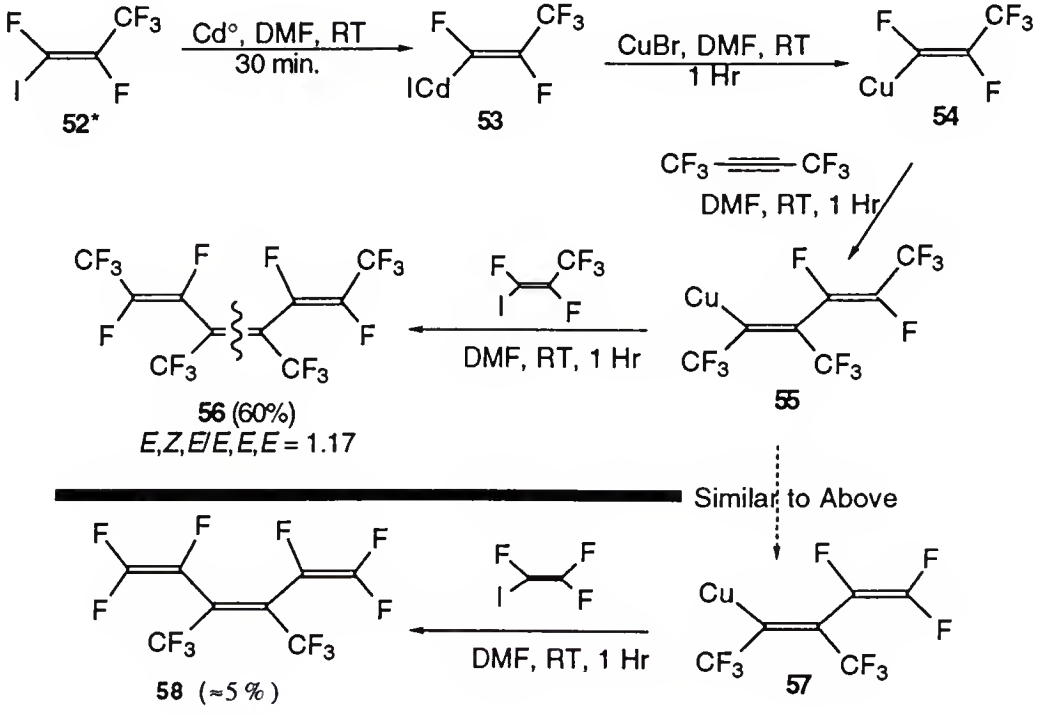


Figure 2-14. Eyring Plots for Separated Rate Constants k_{50} and k_{51}.

in a flow system at 450°C.[69] At this temperature, it is questionable whether this is the primary process involved in this system. A lower temperature, more quantitative study of an acyclic perfluorinated 1,3,5-triene was required.

A system whose synthetic approach potentially allowed for adaptation into a variety of terminally substituted perfluoro-1,3,5-trienes was perfluoro-*E,Z,E*- (and *E,E,E*-)4,5-dimethyl-2,4,6-octatriene (***Z*-56**(***E*-56**)). This system had been previously synthesized and Figure 2-15 illustrates the chemistry involved.[70] This procedure was repeated and the isolated yield and product composition obtained (60%, *E,Z,E*:*E,E,E* = 1.17:1) were similar to those reported (68%, *E,Z,E*:*E,E,E* = 1.63:1).

Initially, an attempt was made to synthesize perfluoro-3,4-dimethyl-1,3,5-hexatriene (**58**) by similar methodology; a process which had been discussed



*Perfluoro-*Z*-1-iodopropene (**52**) was synthesized in four steps from perfluoropropene.[66]

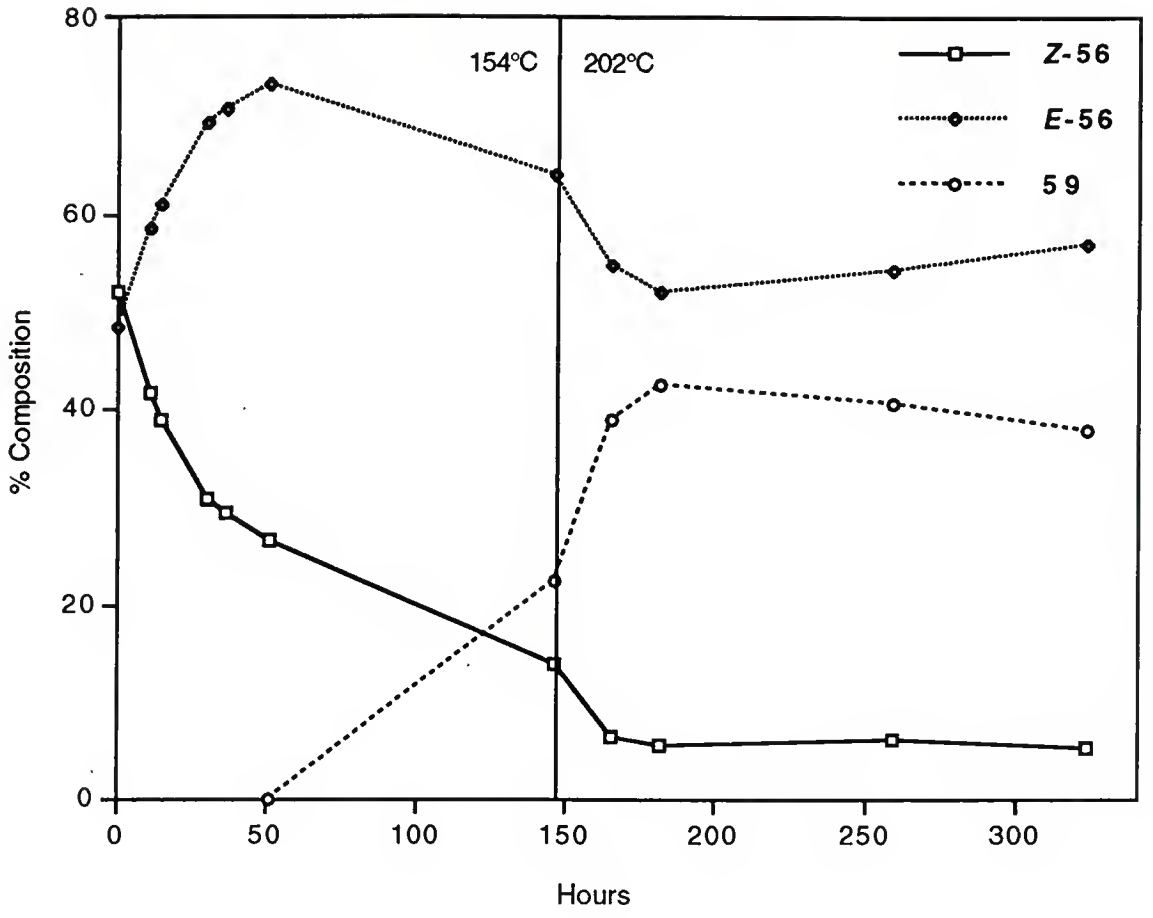
Figure 2-15. Synthesis of Perfluoro-*E,Z,E*(*E,E,E*)-4,5-dimethyl-2,4,6-octatriene (***Z*-56**(***E*-56**)).

only to the point of the chain extended copper reagent **57** in the reference. Following the reaction progress by ^{19}F NMR, formation of **57** was observed, but addition of a further equivalent of iodotrifluoroethylene afforded a 5% or less yield of **52** in the reaction mixture, which for the purpose of this project was synthetically useless. Not having obtained useful quantities of **58**, the synthesis of **56** was repeated and it's thermal chemistry investigated.

The thermolysis of **56** was studied from 149°C to 202°C as a 0.17 M solution in *n*-pentane. Due to difficulty in separation of the triene *E,Z,E* and *E,E,E* isomers, the typical synthetic mixture of isomers (*E,Z,E*:*E,E,E* ratio of 1.17:1) was used in all studies. At temperatures around 150°C, *E,Z,E*→*E,E,E* isomerization was observed to occur. After longer times, one new product was evident, being identified by ^{19}F NMR in the reaction solution as a mixture of perfluoro-*cis*(and *trans*)-1,3,4-trimethyl-4-(*E*-1-propenyl)cyclobutene (**59**). Figure 2-16 shows the percent composition *versus* time for thermolysis of **56** at 154°C and then at 202°C. *E,Z,E*→*E,E,E* isomerization is observed initially followed by appearance of **59** after 50 hours at 154°C. Raising the temperature of the sample to 202°C sets up an equilibrium mixture of ***E*-56/59/*Z*-56** = 11.4/7.6/1. Thus, this system represents a second example where a highly fluorinated 1,3(*Z*),5-triene underwent thermal chemistry other than the 6π disrotatory formation of a 1,3-cyclohexadiene. Since the thermal 6π closure seemed to be disfavored, we were interested to see whether the photochemical 6π conrotatory formation of 1,3-cyclohexadienes would occur in these fluorinated systems.

Photochemical Rearrangements of 9,10-Bis(trifluoroethenyl)phenanthrene (**40**) and Perfluoro-*E,Z,E*(*E,E,E*)-4,5-dimethyl-2,4,6-octatriene (***Z*-56**(***E*-56**))

Upon photochemical excitation, ground state 1,3,5-trienes may undergo



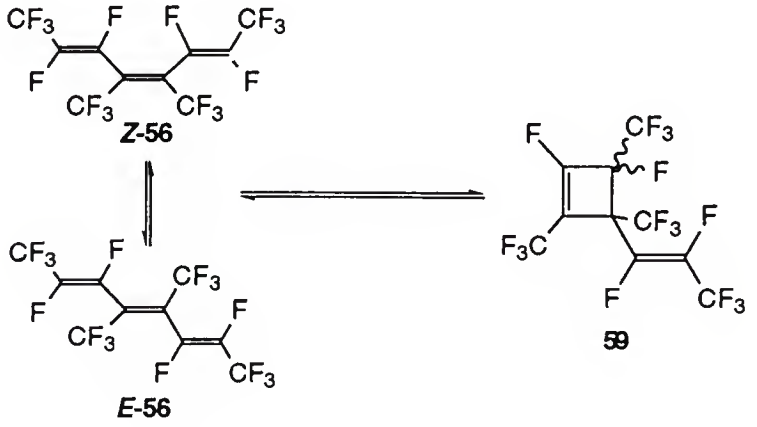


Figure 2-16. Thermolysis of Perfluoro-*E*,*Z*,*E*(*E*,*E*,*E*)-4,5-dimethyl-2,4,6-octatriene (***Z*-56**(***E*-56**)) as a Solution in *n*-Pentane.

π-π^* transformation to singlet excited states.[71] These singlet excited states are biradical in character and create a symmetry change in the 1,3,5-triene HOMO from symmetric in the ground state to antisymmetric in the singlet state. Woodward and Hoffman recognized that concerted photochemical 1,3,5-triene cyclizations and 1,3-cyclohexadiene ring openings occurring by conrotatory processes are an artifact of this change in the HOMO symmetry.[34] More recent theoretical study also recognizes a preferred photochemical conrotatory mode of reaction.[72] Experimentally it is found that the process occurs stereospecifically in a conrotatory fashion as shown in Figure 2-17.[73]

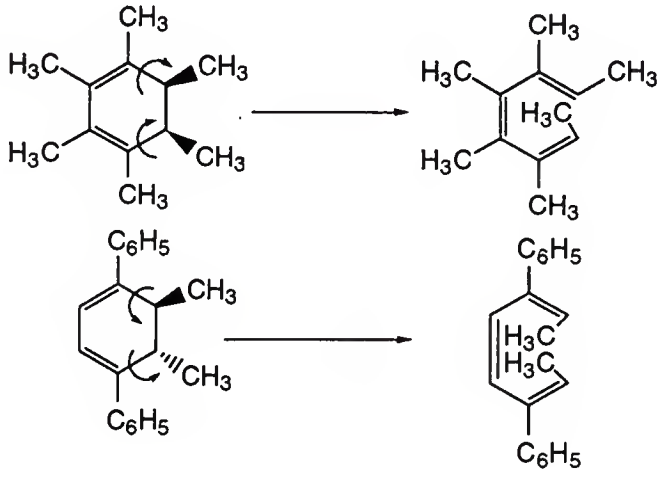


Figure 2-17. Photochemical 6π Conrotatory Processes.

Simple observation of 1,3(*Z*),5-triene/1,3-cyclohexadiene photo-processes are complicated in many cases by other reaction pathways available to the high energy excited state. Figure 2-18 illustrates the variety of products which have been observed in various 1,3,5-triene/1,3-cyclohexadiene photochemical systems.[74] A variety of factors are important in dictating the product distribution and will be discussed later.

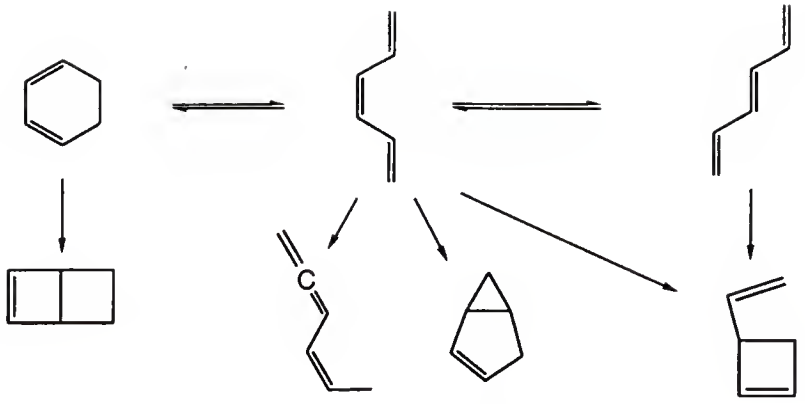


Figure 2-18. Photoproduct Variation in 1,3,5-Triene/1,3-Cyclohexadiene Systems.

Having not observed the thermal 6π disrotatory process to any significant extent in the cases of **40** and ***Z*-56** at the temperatures studied, it was of interest to determine if the photochemical 6π conrotatory process would occur. A question of the relative ability of the two 6π transition states (thermal disrotatory *versus* photochemical conrotatory) to accommodate fluorine emerged, and a qualitative study of the two systems photo-processes was undertaken.

Photolysis of 9,10-Bis(trifluoroethenyl)phenanthrene (**40**)

The photolysis of **40** was studied as a 0.05 M solution in *n*-pentane and the samples were irradiated through Pyrex at room temperature by a heated-cathode, low pressure mercury lamp. Four products are observed to arise from the photolysis of **40**. Figure 2-19 shows the percent composition of all reaction components *versus* solution irradiation time. As found in the thermolysis of **40**, the bicyclo[3.1.0]hex-2-ene **49** is the major product from photolysis of **40**. The 6π electrocyclic product **41** is formed in small and relatively constant concentration throughout the photolysis. Two other [2π+2π] type products,

1,4,5,5,6,6,-hexafluoro-2,3-(9,10-phenanthro)bicyclo[2.1.1]hex-2-ene (**60**) and 1,4,5,5,6,6-hexafluoro-2,3-(9,10-phenanthro)bicyclo[2.2.0]hex-2-ene (**61**) are formed roughly in a ratio of 4.5(**60**):1(**61**) and account for 30% of the reaction mixture after 93% conversion of **40**. Independent photolysis of pure **41** under similar conditions used for **40** led to formation of **61** in low yields; one hour of photolysis of **41** yields 53% **41** remaining and 28% of **61** formed with a 19% decrease in mass balance. Photolysis of **41** for two hours leads to decrease in amounts of all materials and 60% reduction in mass balance. Reversibility of **41** back to triene **40** was not observed to any extent in these studies. Overall photolysis of the parent triene is quite clean and after 21 hours with the aforementioned light source, an 11% decrease in mass balance is observed with 8% **40** remaining. Some extent of polymerization is occurring under these conditions and is revealed by a small amount of solid white film appearing on the walls of the photolysis vessel.

Attempts to isolate **60** and **61** failed. The preparative packed column GLPC conditions necessary to elute these phenanthrene derivatives led to decomposition of **60** and **61**. It was found that thermolysis of a benzene solution containing **49**, **60**, and **61** at 184°C for 83 minutes led to a mixture containing only **41**, **49**, **50**, and **51** with no **60** or **61** remaining and no new products evident. This process was not quantified and other attempts at isolation of **60** and **61** by TLC failed as the isomers could not be separated by this technique.

Photolysis of Perfluoro-*E,Z,E*(*E,E,E*)-4,5-dimethyl-2,4,6-octatriene (***Z*-56**(***E*-56**))

The photolysis of **56** was studied as a 0.17 M solution in *n*-pentane and the samples were irradiated through Pyrex at room temperature using a heated-cathode, low pressure mercury lamp. Two products were observed and

isolated upon photolysis of **56**. Figure 2-20 shows percent composition of all materials *versus* solution irradiation time. Perfluoro-*trans*-2,3,5,6-tetramethyl-1,3-cyclohexadiene (**62**) is the major photoproduct and is accompanied by triene *E,Z,E*↔*E,E,E* C4-C5 double bond isomerization. Perfluoro-*trans*-2,3,5,6-tetramethylbicyclo[2.2.0]hex-2-ene (**63**) is formed in the reaction mixture after longer times and in small quantity when photolysis is carried out through Pyrex. Photolysis of pure **62** through quartz under similar conditions used for **56** leads exclusively to **63**, and ring opening to **56** is not observed to any extent. Attempts to obtain Diels-Alder adducts between **62** and dimethyl acetylenedicarboxylate or N-phenyltriazoline dione in *n*-pentane at temperatures up to 200°C showed no reaction and **62** was also found to be stable at 202°C in *n*-pentane for 18 hours showing no rearrangement or decomposition.

Discussion

The experimental data which have been presented point to an unique disparity in the thermal and photochemical processes occurring in perfluorinated 1,3,5-triene systems. While the observed photochemical products will be shown to have related precedence in hydrocarbon 1,3,5-triene transformations, the thermal rearrangements show little resemblance to those of analogous hydrocarbons. It is recognized that upon such a drastic change as perfluorination, anticipating similar results in these systems as those seen for hydrocarbons is a dangerous assumption. As mentioned earlier, our motivation for study of these perfluorinated systems was that they were easiest to obtain synthetically while offering the widest variety of substitution possibilities, and related precedence had been set in thermal studies of the 4π perfluorinated 1,3-diene/cyclobutene system. The results from photochemical and thermal studies

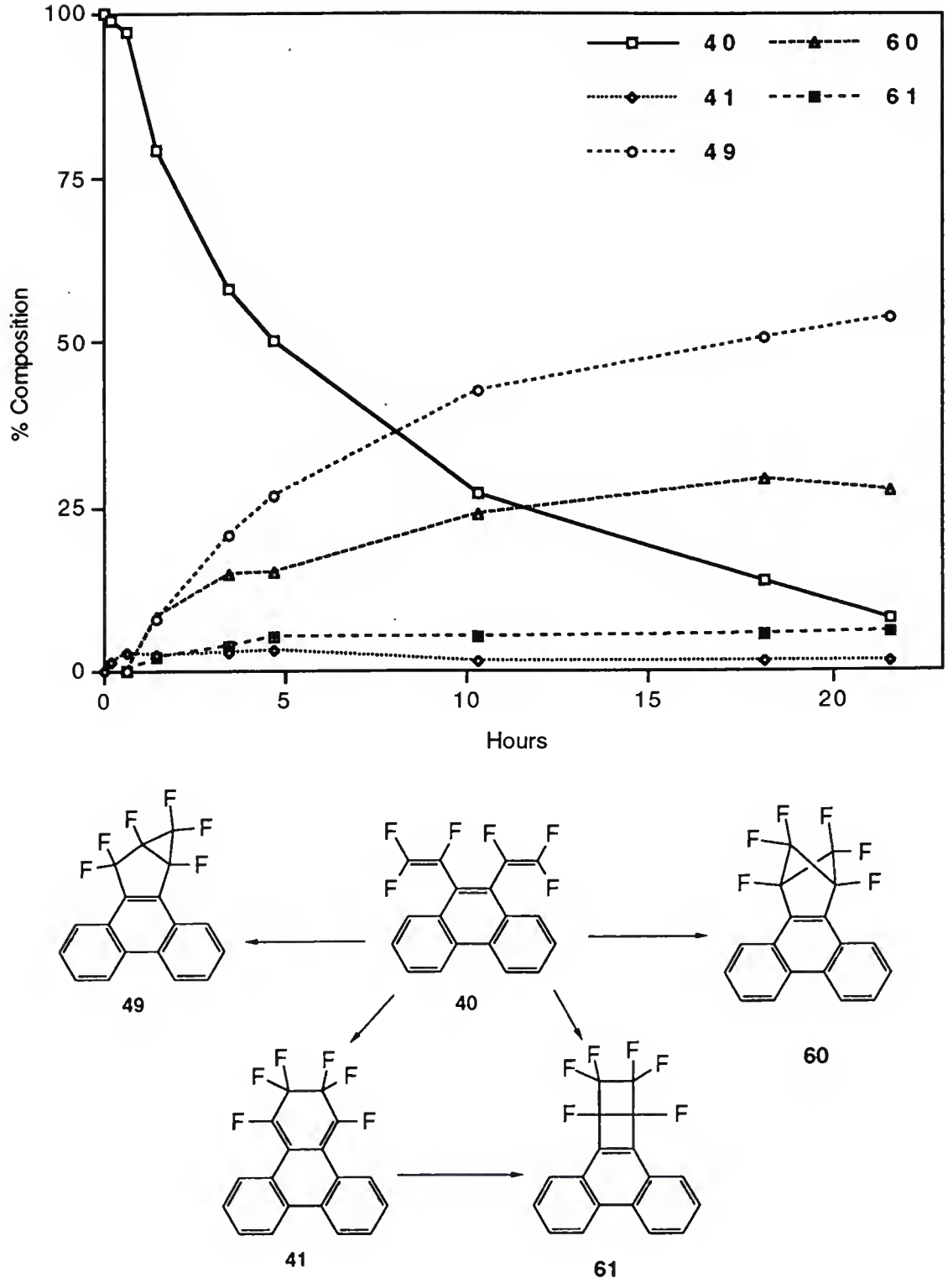
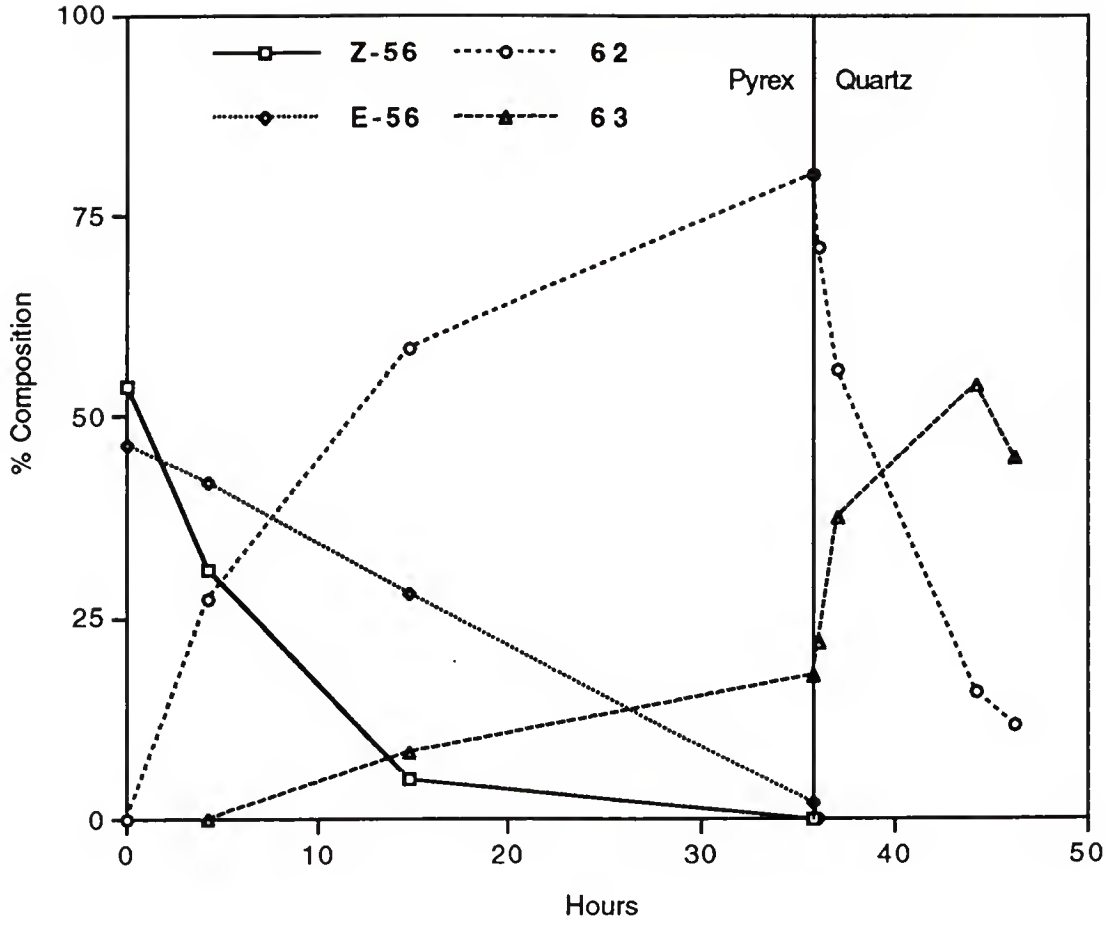


Figure 2-19. Photolysis of 9,10-Bis(trifluoroethenyl)phenanthrene (**40**) as a 0.05 M Solution in *n*-Pentane by Low Pressure Mercury Lamp through Pyrex.



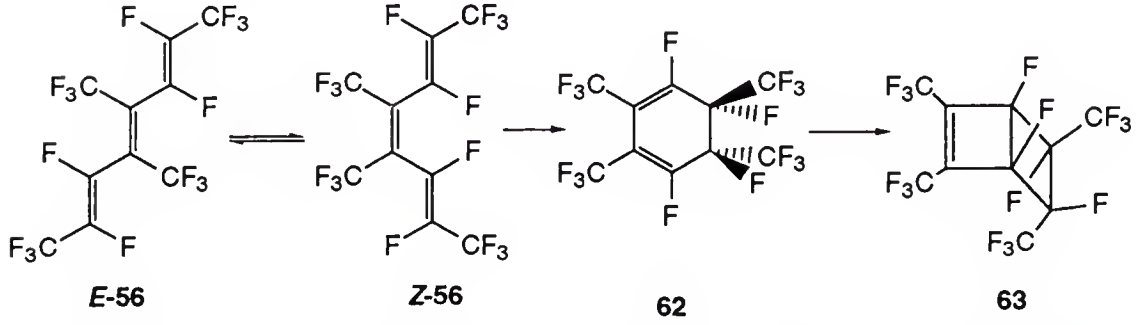


Figure 2-20. Photolysis of Perfluoro-*E*,*Z*,*E*(*E*,*E*,*E*)-4,5-dimethyl-2,4,6-octatriene (***Z*-56**(***E*-56**)) as a 0.17 M Solution in *n*-Pentane by Low Pressure Mercury Lamp.

of perfluoro-*E*,*E*,*E*(*E*,*Z*,*E*)-4,5-dimethyl-2,4,6-octatriene (***Z*-56**(***E*-56**)) and 9,10-bis(trifluoroethenyl)phenanthrene (**40**) will now be discussed in turn.

Discussion of the Photochemical Studies

Early studies in the photochemistry of Vitamin D and it's many isomers set the precedent for the possible complexities of 1,3,5-triene photochemistry.[74] Previously, Figure 2-18 illustrated some of the types of products which have been observed elsewhere in 1,3,5-triene photochemistry.

It is generally accepted that 1,3,5-triene photoproduct composition can be directly related to the ground state conformational distribution of the system by a principle known as the Non-Equilibration of Excited Rotamers (NEER).[74] This principle states that in the excited state, an enhanced barrier for rotation exists about the bonds which in the ground state are single bonds. Due to it's limited lifetime, the acquiring of sufficient thermal energy by the excited state to overcome such a barrier is unlikely. In effect, the photoproduct composition should reflect a quantitative view of the ground state conformational equilibrium which was irradiated. As illustrated in Figure 2-21, the ground state conformations of *Z*-1,3,5-hexatriene will upon irradiation, lead in a specific fashion to NEER dictated products.[74]

Although a seemingly trivial concept, the NEER principle turns out to have good predictive value. Methods such as ^{1}H NMR and UV spectroscopy have been used to establish the preferred conformation in some hydrocarbon 1,3,5-trienes such as **64**,[75,76] and **65-67**,[74,77] and the corresponding 254 nm primary photoproducts are shown in Figure 2-22. Absolute proof of an mechanistic rationale is difficult and more so in the case of NEER because of the number of relevant untested variables and alternate mechanistic proposals. The possibility of equilibration of excited conformers has been addressed and

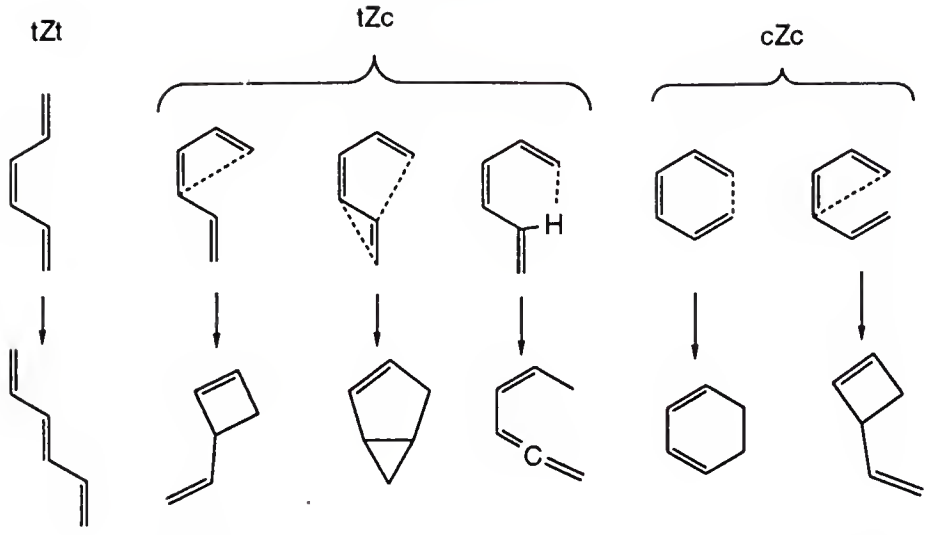


Figure 2-21. Three "Planar" Conformations of *Z*-1,3,5-Hexatriene and Corresponding Photoproducts.

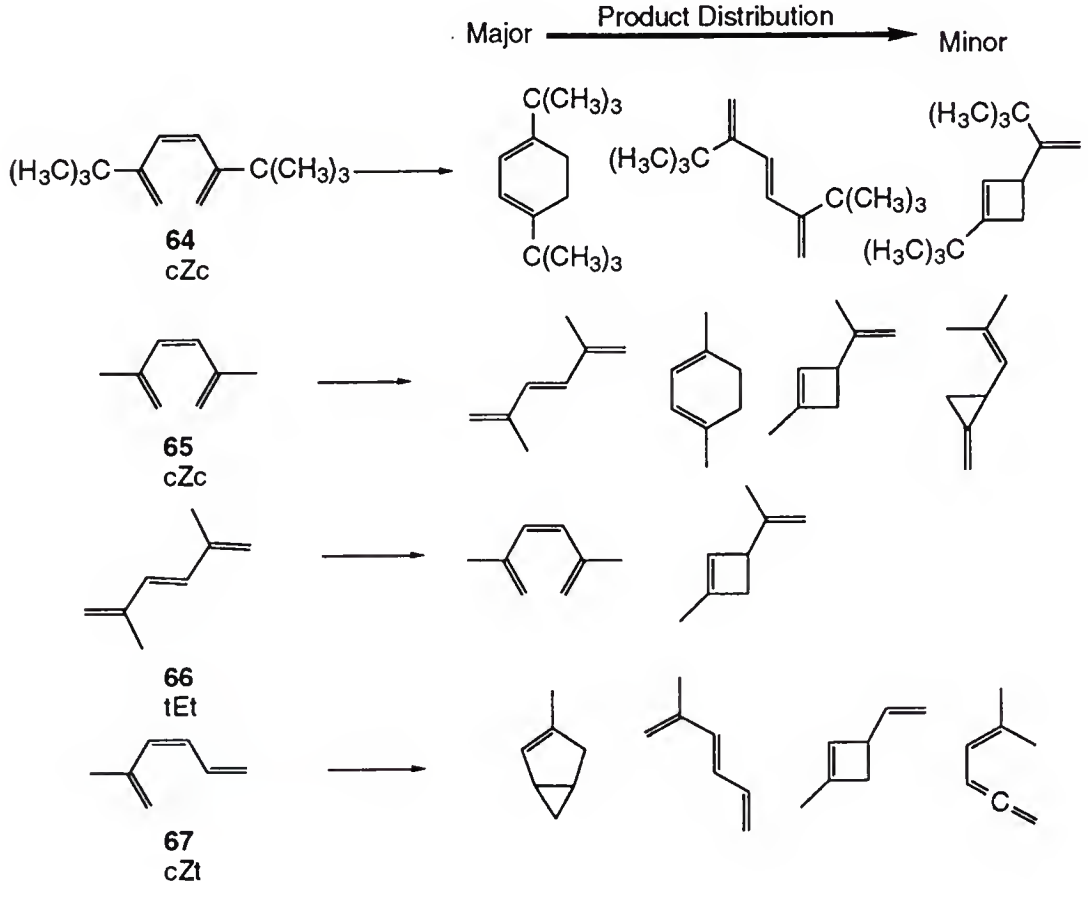
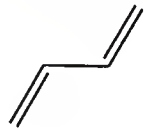
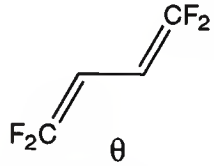
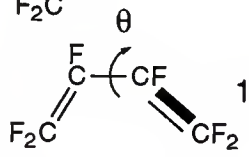


Figure 2-22. Examples of 1,3,5-Triene Preferred Ground State Conformations and 254 nm Primary Photoproduct Distribution.

dismissed by a study of the influence of wavelength on the photoproduct distribution at low percentage conversion.[74,78]

The preferred ground state conformation of acyclic 1,3,5-trienes changes considerably from the hydrocarbon to perfluorocarbon systems. A variety of studies (UV and photoelectron spectra[79], theoretical consideration[60,80]) point toward perfluoro-1,3-butadiene (**75**) existing in a *cis*-skew structure with torsion angle θ = 42° (Figure 2-23), whereas 1,3-butadiene (**73**) exists in a planar *trans* conformation with θ = 180°. A significant hypsochromic shift is observed as the series of fluoroethylenes (**68 - 72**) is transversed. This trend is also observed between **73**, **74**, and **75**, but here along with photoelectron spectral data, is

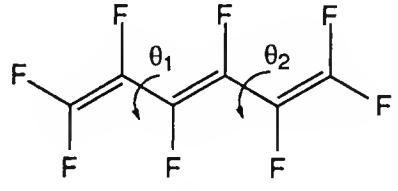
		λ_{max} (nm)	E_{max} (L/molxcm)	θ (deg)
68	$H_2C{=}CH_2$	165	10,000	-
69	$H_2C{=}CHF$	167	10,000	-
70	$H_2C{=}CF_2$	165	7,900	-
71	$FHC{=}CF_2$	162	6,800	-
72	$F_2C{=}CF_2$	139	11,370	-
73		210	22,300	180°
74		200	19,500	180°
75		162	6,800	42°

References: **68**[21], **69-72**[81], **73**[82], **74**[79], **75**[82]

Figure 2-23. UV Data for Fluoroethylenes and Fluorobutadienes.

proposed to be due to non-planarity in **75** relative to **73** and **74**.[79] Perfluoro-1,3-butadiene (**75**) is observed to have a UV spectrum identical with $HFC=CF_2$ (**71**), further indicating there is little interaction between the C1-C2 and C3-C4 π systems. This non-planarity is displayed by models where a disadvantageous interaction is observed between fluorines on C1 and C3, and C2 and C4 in the planar *trans* conformation.[83] Hypsochromic shifts attributed to non-planarity have been observed in other non-planar polyenes such as 2,3-di-*t*-butylbutadiene, where λ_{max} = 186 nm.[84]

Perfluoro-*E*-1,3,5-hexatriene (***E*-76**) has been subjected to theoretical conformational study at the *ab initio* level.[60] Two torsional angles (θ_1, θ_2) exist in this molecule and local minima were located for two structures with *syn* and *anti* relations of the pendant alkenes relative to the plane formed by C2-C3-C4-C5. Figure 2-24 illustrates the conformers and the relative energies calculated. The lowest energy conformer of ***E*-76** was found to be a *syn*-skew structure as is observed with perfluoro-1,3-butadiene (Figure 2-23, **75**).



***E*-76**

θ_1 (deg)	θ_1 (deg)	ΔE (kcal/mol)
180	180	3.10
146	-146	2.29
146	146	2.01
53	-53	0.10
52	52	0.00

Figure 2-24. Relative Calculated Minima for Perfluoro-*E*-1,3,5-hexatriene (***E*-76**).

Photochemical Study of Perfluoro-*E,Z,E*-(and*E,E,E*)4,5-dimethyl-2,4,6-octatriene (***Z*-56**(***E*-56**))

Photolysis of perfluoro-*E,Z,E*-4,5-dimethyl-2,4,6-octatriene (***Z*-56**) and perfluoro-*E,E,E*-4,5-dimethyl-2,4,6-octatriene (***E*-56**) yielded only two products; perfluoro-*trans*-2,3,5,6-tetramethyl-1,3-cyclohexadiene (**62**) and perfluoro-*trans*-1,2,3,4-tetramethylbicyclo[2.2.0]hex-2-ene (**63**) in good yield. The overall transformation is illustrated in Figure 2-25. Triene ***E*-56** has two possible modes of reaction available by NEER type reasoning; 4π disrotatory ring closure or C4-C5 double bond isomerization. The lowest energy conformer for ***E*-56** will most likely be similar to that of ***E*-76**, a skewed non-planar structure. The 4π disrotatory photo-process leading to a 3-propenylcyclobutene would require a t*E*c triene conformer which would be disfavored due to a repulsive interaction between C2 fluorine and C5 trifluoromethyl groups. Therefore, the observed process for ***E*-56** is *E,E,E*→*E,Z,E* isomerization about the C4-C5

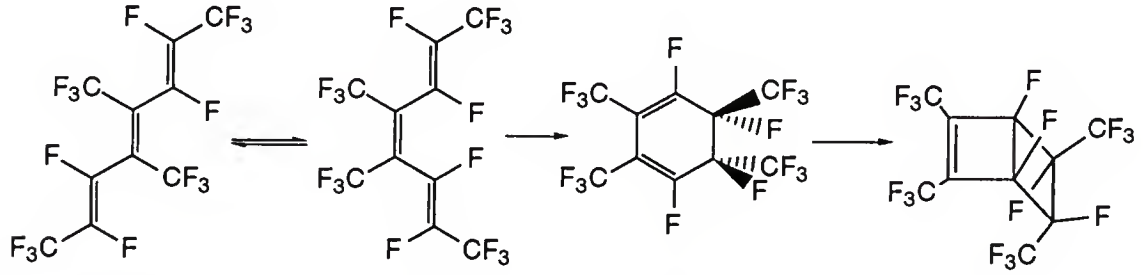


Figure 2-25. Photolysis of Perfluoro-*E,Z,E*(*E,E,E*)-4,5-dimethyl-2,4,6-octatriene (***Z*-56**(***E*-56**)).

double bond to form ***Z*-56**. *Cis* triene ***Z*-56** is found to undergo only 6π conrotatory closure to yield **62**. The lowest energy conformer of ***Z*-56** most likely involves skewing of the pendant *E*-perfluoropropenyl groups relative to the C3-C4-C5-C6 plane, but whether it exists *cis* or *trans* skewed about the C3-C4 and C5-C6 single bonds is unknown. It is noticed that a *cis* skewed

structure of ***Z*-56** (Figure 2-26) is perfectly aligned with minimal repulsion to undergo allowed 6π conrotatory bond formation between C2 and C7 leading directly to **62**.

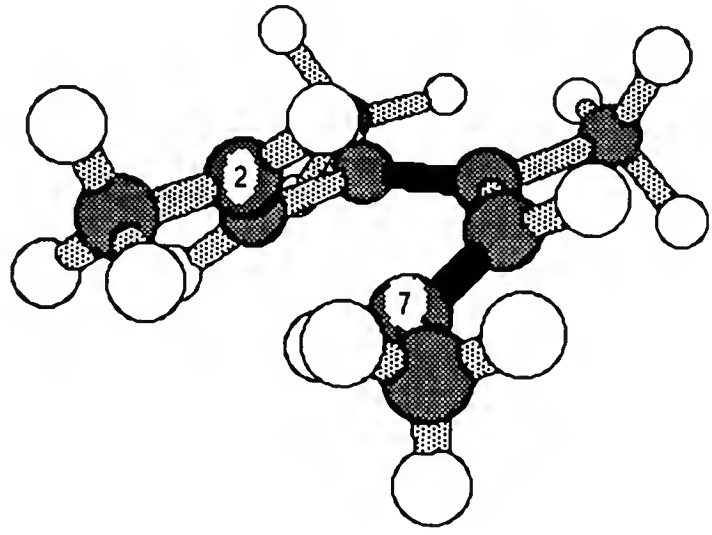


Figure 2-26. *Cis*-Skewed Conformer of Perfluoro-*E,Z,E*-4,5-dimethyl-2,4,6-octatriene (***Z*-56**).

Perfluoro-*trans*-2,3,5,6-tetramethyl-1,3-cyclohexadiene (**62**) undergoes a further formal 4π disrotatory closure to form perfluoro-*trans*-1,2,3,4-tetramethyl-bicyclo[2.2.0]hex-2-ene (**63**) in preference to ring opening to perfluoro-*E,Z,E*-4,5-dimethyl-2,4,6-octatriene (***Z*-56**). Using experimental results and NEER type reasoning, it has been established for hydrocarbon photochemical 1,3-cyclohexadiene processes that the preferred ground state conformation of the system will control whether the 6π conrotatory ring open 1,3(*Z*),5-triene or 4π disrotatory ring closed bicyclo[2.2.0]hex-2-ene is observed.[85] Studies have shown that planar or half-boat type conformers (Figure 2-27) undergo disrotatory closure to bicyclo[2.2.0]hex-2-enes and half-chair type conformers prefer conrotatory ring opening to 1,3(*Z*),5-trienes.

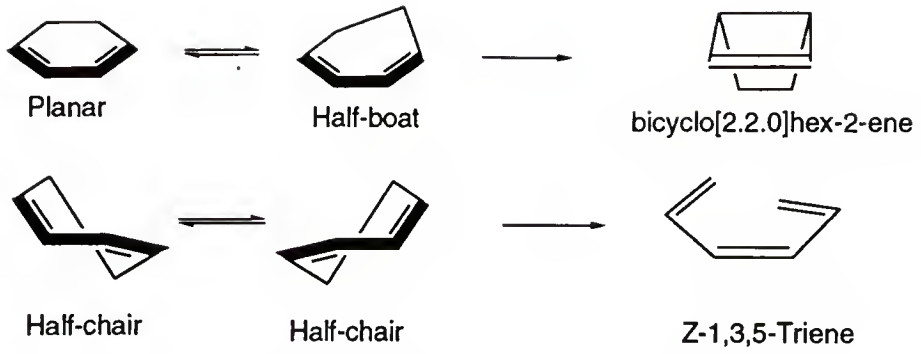


Figure 2-27. Conformationally Controlled Photo-processes of 1,3-Cyclohexadienes.

With this precedent, it is surprising that cyclohexadiene **62** does not undergo ring opening. Model studies[83] indicate the most favored conformer of **62** (Figure 2-28) is one in which trifluoromethyl steric repulsions are minimized in a half chair ring orientation with di-pseudoaxial C5 and C6 trifluoromethyl groups and a C1-C2-C3-C4 torsion angle larger than that found in 1,3-cyclohexadiene.

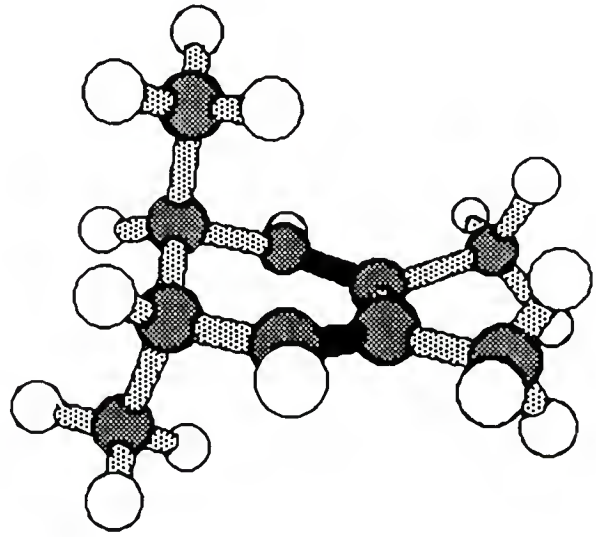


Figure 2-28. Favored Half-Chair Conformer of Perfluoro-*trans*-2,3,5,6-tetramethyl-1,3-cyclohexadiene (**62**).

The photochemical results obtained with fluorinated triene **56** are consistent with the few other fluorinated examples found in the literature. Recently, it has been reported that perfluoro-*Z*-1,3,5-hexatriene (***Z*-76**) undergoes double bond isomerization and 4π and 6π photoclosures (Figure 2-29) to yield a mixture of perfluoro-*E*-1,3,5-hexatriene (***E*-76**), perfluoro-1,3-cyclohexadiene (**77**) and perfluoro-3-ethenylcyclobutene (**78**).[86] At low percent conversions of ***Z*-76**, only ***E*-76** and **77** are identified in the reaction mixture. When the reaction is carried out to completion a mixture containing 25% **77**, 40% **78**, and 35% perfluoro[2.2.0]bicyclohex-2-ene (**79**) is obtained.

An inconsistency exists in that the formation of the perfluoro-3-ethenylcyclobutene (**78**) ring structure was not observed in the case of **56**. As already discussed, ***E*-56** will not populate the t*Z*c conformation for steric reasons and undergoes *E,E,E*→*E,Z,E* isomerization only. It is difficult to see why ***Z*-56** is not observed to form 4π cyclization products as are observed in the

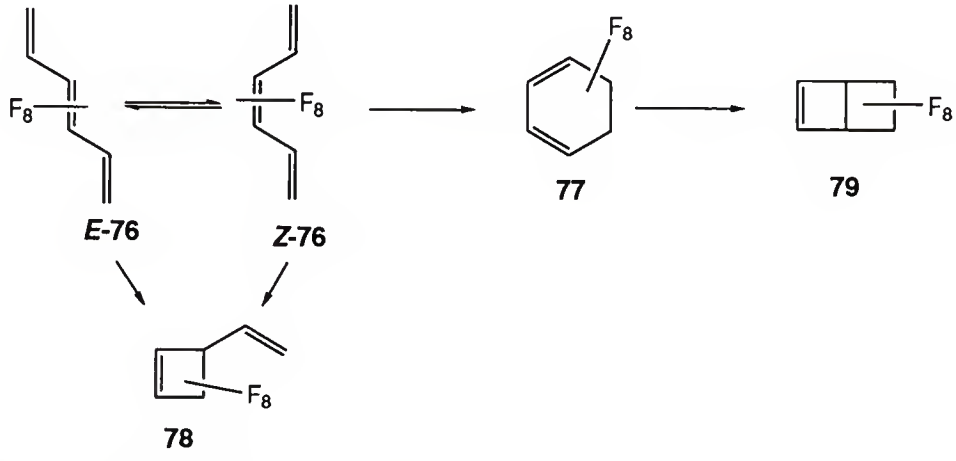


Figure 2-29. Photoproducts Obtained from Perfluoro-*Z*-1,3,5-hexatriene (**Z-76**).

case of ***Z*-76**. Models indicate the c*Z*t conformation of ***Z*-56** may exist as it must for ***Z*-76** with little crowding of the trifluoromethyl substituents. A possible explanation arises if one assumes only the fluorinated *E*-trienes are undergoing

the 4π cyclization. In this case, c*E*t ***E*-76** can undergo 4π closure or *E*→*Z* isomerization, whereas t*E*t ***E*-56** affords only ***Z*-56**. It is unproved whether such an argument applies, but if so, it would be unique to these perfluorinated 1,3,5-trienes as both *E* and *Z* hydrocarbon 1,3,5-trienes are observed to form 3-alkenylcyclobutenes as primary photoproducts (Figure 2-22).

Photolysis of perfluoro-1,3-cyclohexadiene (**77**) using a low pressure mercury lamp has been previously reported to quantitatively yield **79** as the sole photoproduct.[87] In contrast to the previous fluorinated 1,3-cyclohexadiene results, photolysis of perfluorotricyclo[6.2.2.$0^{2,7}$]dodeca-2,6,9-triene (Figure 2-30, **80**) yields bicyclo[3.1.0]hex-2-ene type isomers **82** and **83**. These products are proposed to be originating from the ring opened triene **81**, a species which was never observed in this study.[88] Due to the rigidity of the bicyclohexene ring structure of **80**, the cyclohexadiene ring will be very nearly planar. The formation of 1,3,5-hexadiene **81** goes counter to the NEER predicted product for this system, which would be formation of a bicyclo[2.2.0]hex-2-ene (Figure 2-27) type ring structure.

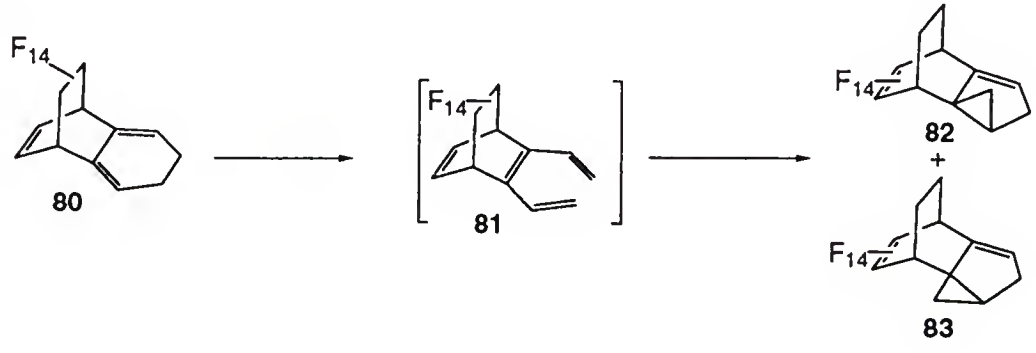


Figure 2-30. Photolysis of Perfluorotricyclo[6.2.2.$0^{2,7}$]dodeca-2,6,9-triene (**80**).

Photochemical Study of 9,10-Bis(trifluoroethenyl)phenanthrene (**40**)

Photolysis of 9,10-bis(trifluoroethenyl)phenanthrene (**40**) led to formation of four structural isomers; **41**, **49**, **60**, and **61** as illustrated in Figure 2-31.

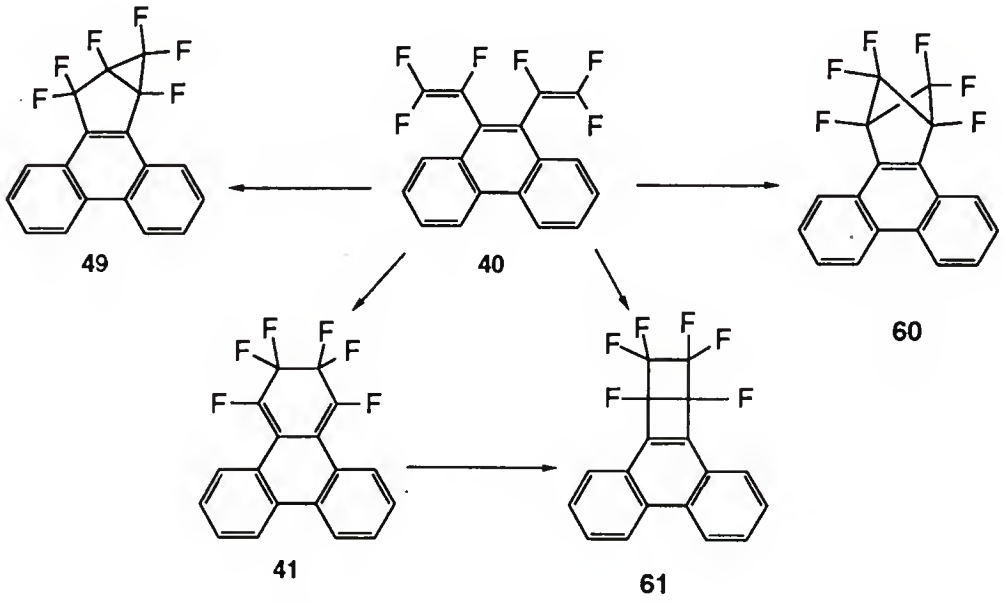
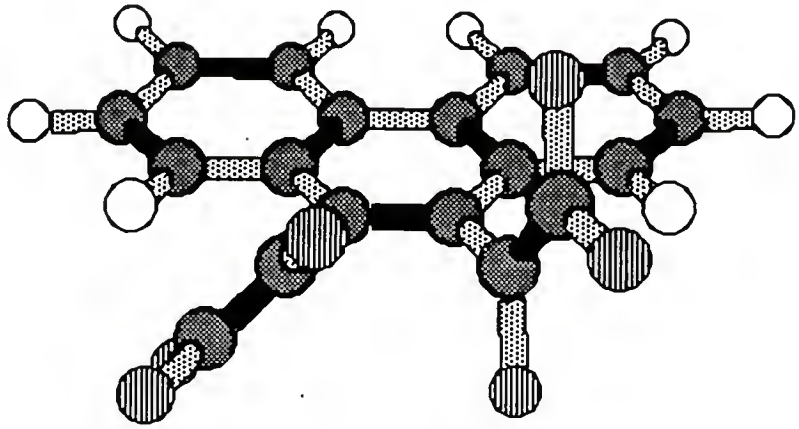


Figure 2-31. Photolysis of 9,10-Bis(trifluoroethenyl)phenanthrene (**40**).

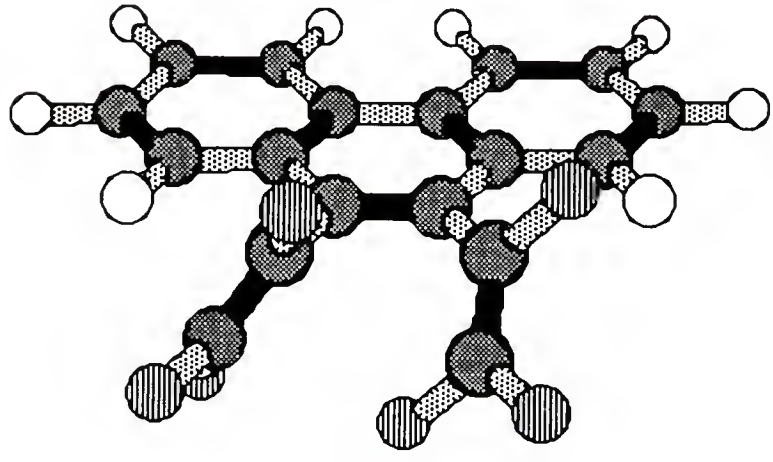
9,10-Bis(trifluoroethenyl)phenanthrene (**40**) was observed by ^{19}F NMR to exist as a pair of torsional diastereomers with a substantial energy barrier to interconversion, a discussion of which has been published.[89] The ^{19}F NMR spectrum of **40** at 25°C showed signals corresponding to two types of non-equivalent trifluoroethenyl groups. Such a spectrum is believed to arise from a substantial thermal barrier due to restricted rotation between conformers involving an *syn* and *anti* relationship of the trifluoroethenyl substituents relative to the plane of the phenanthrene ring. Observation of the ^{19}F NMR spectra of **40** over the temperature range of -17°C to 84°C and application of classical theory with respect to equilibrium and NMR spectra allowed an estimation of $\Delta G^{\ddagger} \approx 15$ kcal/mol for interconversion of the isomers. Molecular mechanics

calculations estimated $\Delta H°_{Rxn}$ = 0.7 kcal/mol for ***anti*-40→*syn*-40** with $\Delta H^{\ddagger}$ = 16.01 kcal/mol.[90] Local minima for *syn* (***syn*-40**) and *anti* (***anti*-40**) type conformers were located (Figure 2-32) with trifluoroethenyl torsional angles relative to the aromatic ring plane (tZt structure) for the *anti* conformer of 50° and -75°, and for the *syn* conformer of 62° and 119°.



***anti*-40**

$K_{(syn/anti)}$ = 0.48, $CDCl_3$, 25°C



***syn*-40**

Figure 2-32. Conformational Equilibrium of 9,10-Bis(trifluoroethenyl)-phenanthrene (**40**).

The formation of the observed photoproducts from **40** has some precedent from the hydrocarbon literature. Photochemical studies of 1,2-diethenylbenzene (**84**, Figure 2-33) have been reported by a few authors.[91,92,93] One study found that photolysis of **84** with a medium pressure mercury arc through Pyrex yielded benzobicyclo[3.1.0]hex-2-ene (**83**) as the major product in a low overall yield process (20% max) with smaller amounts of tetralin, 1,2-dihydronaphthalene, and naphthalene observed arising from 2,3-dihydronaphthalene (**85**).[91] 1,2-Diethenylbenzene-d_4 with four terminal methylene deuterons was also studied to establish a carbon skeletal rearrangement *via* **86** to **83**, disproving a mechanism involving hydrogen migration.[91]

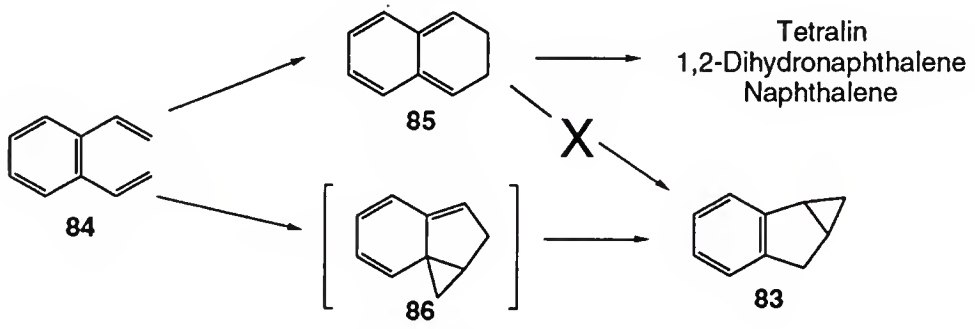
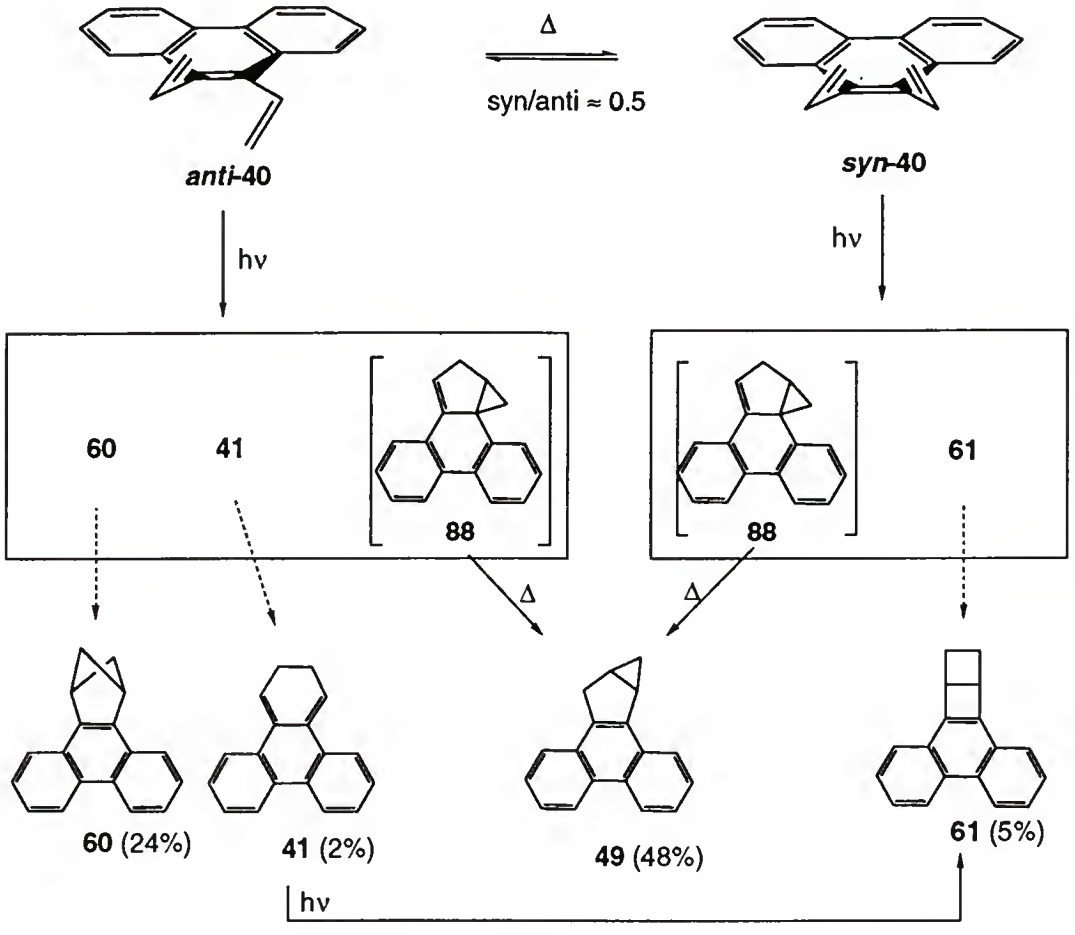


Figure 2-33. Photolysis of 1,2-Diethenylbenzene (**84**).

Photolysis of 9,10-diethenylphenanthrene has been reported and studies under a variety of conditions did not lead to the observation of any cyclization.[94] In this case, polymerization was the only process which was observed.

The photoproducts observed from 9,10-bis(trifluoroethenyl)phenanthrene (**40**) are consistent with the above hydrocarbon system results and they can potentially be seen as arising from a NEER dictated process. Figure 2-34 shows the proposed overall primary and secondary processes. Conformer ***anti*-40** can form three primary photoproducts; **41**, **60**, and **88**.

Bicyclo[2.1.1]hex-2-ene **60** may be formed from the pendant alkenes reacting in a photo-allowed $2_{\pi}s+2_{\pi}s$ cycloaddition and cyclohexadiene **41** may arise from a 6π conrotatory electrocyclization. Initial formation of bicyclo[3.1.0]hex-2-ene **88** may occur through either the ***anti*-40** or ***syn*-40** conformers and the true nature of the photochemical mechanism involving formation of bicyclo[3.1.0]hex-2-enes has been the subject of much debate.



*All bonds to fluorine except for the 1 through 8 positions of the phenanthrene ring systems.

Figure 2-34. Primary and Secondary Processes and Final Product Distribution for Photolysis of 9,10-Bis(trifluoroethenyl)phenanthrene (**40**).

Photochemical formation of bicyclo[3.1.0]hex-2-enes are formally Woodward and Hoffman allowed $4_{\pi}s+2_{\pi}a$ or $4_{\pi}a+2_{\pi}s$ processes.[34] Establishing

the true nature of the mechanism requires labels with which to follow the stereochemical course of the process. While there are examples of $4_\pi s+2_\pi a$ and $4_\pi a+2_\pi s$ photoisomerizations,[95,96] there are also examples of disallowed $4_\pi a+2_\pi a$ processes.[97] Further, an explanation exists based on "cross-bicyclization in linear conjugated polyenes" where the author's rationalization allows for concerted $4_\pi a+2_\pi a$ photo-processes.[98] Other arguments have involved a stepwise process which involves a concerted conrotatory closure of the three membered ring followed by closure of the five membered ring,[85,99] and sudden polarization of the 1,3(*Z*),5-triene from a C3-C4 twisted diradical to a charge separated zwitterion which undergoes closure.[100,101,102]

Primary photoproduct **88** was never observed most likely due to thermal instability caused by strain in this spiro-fused system and loss of aromaticity from the central phenanthrene ring. Under the reaction conditions, **88** most likely undergoes a vinylcyclopropane-cyclopentene rearrangement to **49** as rapidly as it is formed. Photolysis of **40** was attempted at -50°C looking for **88** by low temperature ^{19}F NMR but only **49** was observed. Lower temperature studies were abandoned due to equipment difficulties. Bicyclo[2.2.0]hex-2-ene **61** may be formed by a photo-allowed $2_\pi s+2_\pi s$ cycloaddition from ***syn*-40** or a secondary process involving a 4π disrotatory electrocyclization of **41**. This was found to be occurring as photolysis of pure samples of **41** led in low yield to **61** and showed no reversibility to the parent triene **40**.

Discussion of Thermal Studies

The initial assumption that a suitably tailored fluorinated 1,3(*Z*),5-triene system would allow for probing of the torquoelectronic effect in triene 6π thermal chemistry turned out to be incorrect in the case of the phenanthrene annulated system. Investigation of the thermal rearrangements of 9,10-bis(trifluoro-

ethenyl)phenanthrene (**40**) and perfluoro-*E,Z,E*(and *E,E,E*)-4,5-dimethyl-2,4,6-octatriene (***Z*-56**(***E*-56**)) revealed that rearrangement pathways for these systems have little in common with the corresponding hydrocarbons.

Thermolysis of Perfluoro-*E,Z,E*(and *E,E,E*)-4,5-dimethyl-2,4,6-octatriene (***Z*-56**(***E*-56**)

Thermolysis of the mixture of ***Z*-56** and ***E*-56** led to initial C4-C5 *Z/E* double bond isomerization at temperatures above 150°C. The hydrocarbon analog, *Z*-1,3,5-hexatriene, forms 1,3-cyclohexadiene with E_a = 29.3 kcal/mol, while C3-C4 *E* to *Z* double bond isomerization requires temperatures in excess of 250°C with E_a = 45.5 kcal/mol.[57] Thus, the hydrocarbon *Z*-triene undergoes the 6π electrocyclic process exclusively due to the $\Delta E_a \approx 16$ kcal/mol difference between it's concerted ring closure and it's C3-C4 double bond isomerization. Although alkyl substitution can lower the E_a for C3-C4 double bond isomerization of 1,3,5-hexatriene by approximately 6 kcal/mol[57] and perfluorination of 2-butene leads to a lowering of the $E \leftrightarrow Z$ isomerization by 6.4 kcal/mol versus the hydrocarbon,[103] it is inconceivable that the fluorination of ***Z*-56** will lead to lowering in energy of the C4-C5 double bond $Z \rightarrow E$ isomerization so as to make this process exclusively preferred over the 6π ring closure.

The next process observed to occur is a 4π cyclization of triene **56**. An equilibrium ratio of 1.64:1 was established between **56** (***E*** and ***Z***) and **59** at 202°C in *n*-pentane as illustrated in Figure 2-35.

Perfluoro-1,3,5-hexatriene (**76**) has been reported in a patent to afford an 84% yield of perfluoro-1,3-cyclohexadiene (**77**) upon pyrolysis at 450°C in a flow system.[69] Concurrent to this thesis project, a thermal study of perfluoro-1,3,5-hexatriene at lower temperatures was reported.[86] These authors offered similar results to those obtained in our study of **56**. Thermolysis of

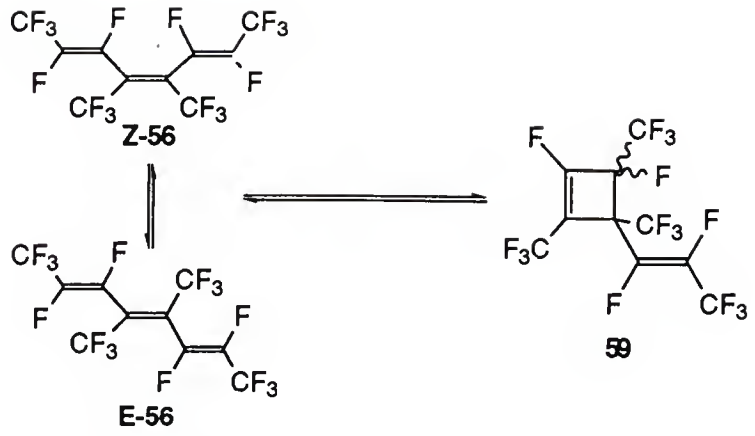


Figure 2-35. Mixture Obtained from Thermolysis of Perfluoro-*E*,*Z*,*E*(*E*,*E*,*E*)-4,5-dimethyl-2,4,6-octatriene (***Z*-56**(***E*-56**)) at 202.0°C in *n*-Pentane.

perfluoro-1,3,5-hexatriene at 160°C established an equilibrium mixture consisting of 9% perfluoro-1,3,5-hexatriene and 90% perfluoro-3-ethenylcyclobutene (**78**). Thermolysis of perfluoro-1,3,5-hexatriene at 220°C was reported to irreversibly yield perfluoro-1,3-cyclohexadiene.

In the fluorinated 1,3,5-triene systems, formation of 3-alkenylcyclobutenes in preference to 1,3-cyclohexadienes upon thermolysis leads to the conclusion that the energy surfaces for the hydrocarbon and fluorocarbon systems are quite different. It is informative to observe the enthalpy diagram (Figure 2-36)[57] for the hydrocarbon C_6H_8 system. Formation of 3-ethenylcyclobutene (**89**) by a 4π conrotatory electrocyclic process is not observed in hydrocarbon 1,3,5-triene thermal studies. *E*-1,3,5-Hexatriene (**36**) isomerizes to the *Z*-triene (**37**) which then undergoes the 6π ring closure to 1,3-cylohexadiene (**38**). Both processes are preferred over the 4π cyclization. Perfluoro-1,3,5-hexatriene is seen to form perfluoro-1,3-cyclohexadiene at higher temperatures and it is likely that perfluoro-*E*,*Z*,*E*-4,5-dimethyl-2,4,6-octatriene (***Z*-56**) would have exhibited a similar reaction path had the system been investigated at higher temperatures.

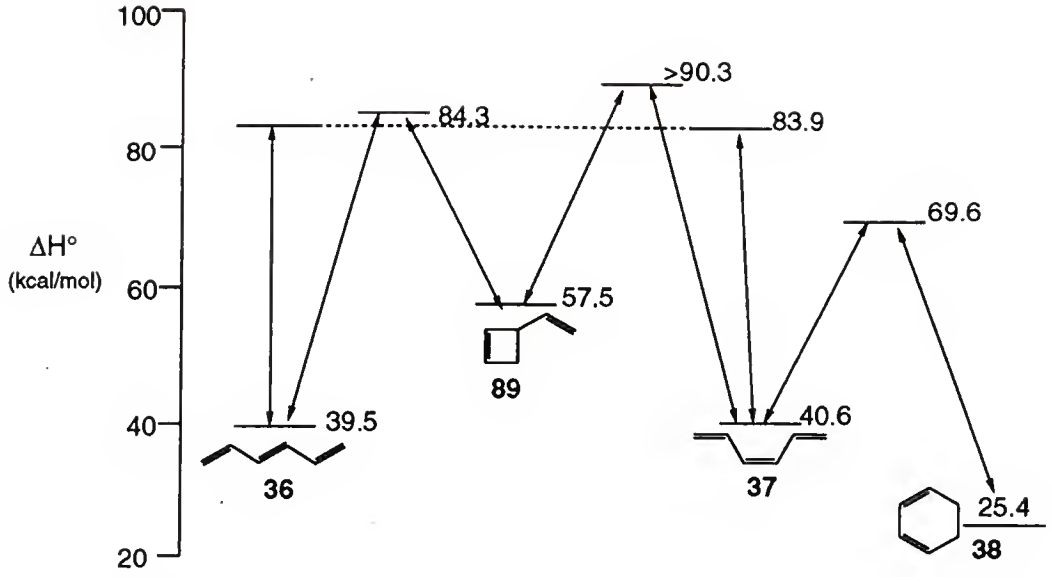


Figure 2-36. Enthalpy Diagram for C_6H_8 Transformations.

The data obtained from these perfluoro-1,3,5-triene systems, although qualitative in nature, require changes in the energy profile for fluorinated 1,3,5-triene transformations (Figure 2-37). The thermal equilibrium rich in perfluoro-3-alkenylcyclobutenes in the cases of perfluoro-1,3,5-hexatriene (**76**) and perfluoro-*E*,*Z*,*E*(and *E*,*E*,*E*)-4,5,-dimethyl-2,4,6-octatriene (***Z*-56**(***E*-56**)) lead to a lowering of the $\Delta H°_F$ of the perfluoro-3-alkenylcyclobutenes relative to the perfluoro-1,3,5-trienes. Such a change in the relative enthalpy has precedent in the case of the earlier discussed fluorinated cyclobutene/1,3-diene interconversions (Chapter One, Table 1-6 and Figure 1-12). In these examples, it was found that the perfluorinated cyclobutenes were lower in energy than the perfluoro-1,3-dienes with $\Delta\Delta H°_R$ on the order of 17 kcal/mol between the hydrocarbon and fluorocarbon systems. Irreversible formation of perfluoro-1,3-cyclohexadienes from the fluoro-1,3(*Z*),5-trienes only in the high temperature runs leads to these species having the most negative $\Delta H°_F$ of the isomers, but with a raised energy barrier to the 6π disrotatory transition state.

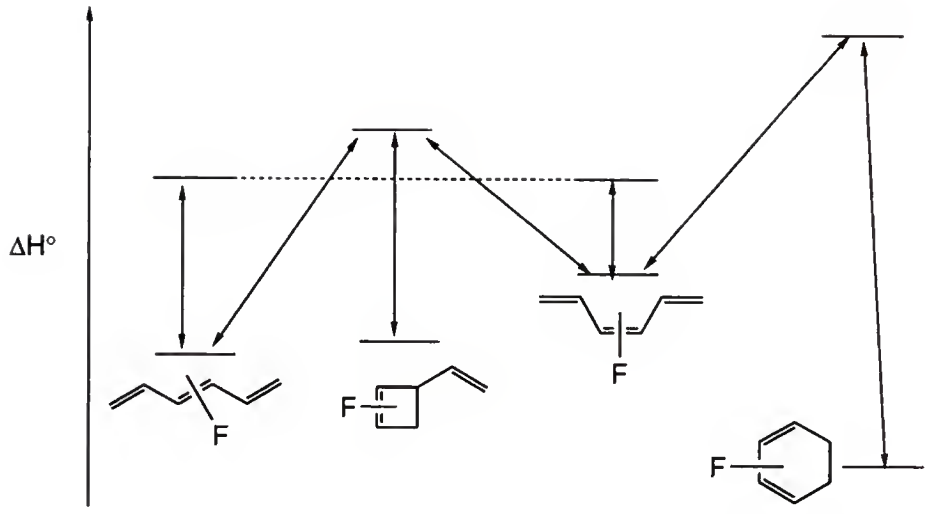


Figure 2-37. Enthalpy Diagram for Perfluoro-1,3,5-triene Transformations.

Thermolysis of 9,10-Bis(trifluoroethenyl)phenanthrene (**40**)

Thermolysis of 9,10-bis(trifluoroethenyl)phenanthrene (**40**) was found to form the desired 1,2,2,3,3,4-hexafluoro-2,3-dihydrotriphenylene (**41**), but only as a small component in a very complicated overall reaction process. A virtually unprecedented process for 1,3(*Z*),5-triene thermal chemistry, leading to bicyclo[3.1.0]hex-2-ene **49** and subsequent rearrangement of this species, was observed to comprise the major reaction pathway of **40**.

Thermal studies of 1,2-dialkenyl aromatics are only rarely encountered in the literature. Any attempt to investigate the electrocyclic chemistry of such systems would be expected to be complicated by the instability of the cyclized non-aromatic products under the reaction conditions and the facility of these products to undergo further rearrangement. Thermal studies of a series of 1,2-dipropenylbenzenes has been reported.[104] These systems first show pendant alkene isomerization which was proven to occur by [1,7]-sigmatropic hydrogen shifts. Higher temperatures yield 1,2-dihydronaphthalenes and alkyl 1,2-dihydronaphthalenes which arise from disrotatory ring closure followed by an

[1,5]-sigmatropic hydrogen shift. The mechanistic nature of these processes was established by studying suitably deuterium labeled species, and a mechanistic rationale was proposed as seen in Figure 2-38.[104]

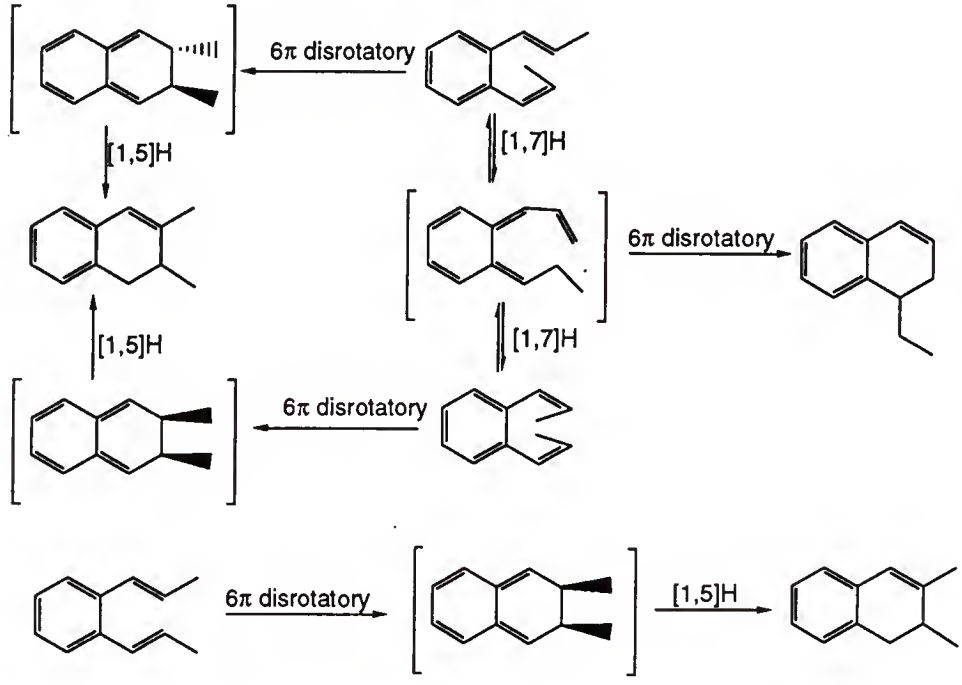


Figure 2-38. Thermal Processes Observed for 1,2-Dipropenylbenzenes.

One instance of the thermolysis of 9,10-diethenylphenanthrene at 210°C has been reported to yield 35% triphenylene, apparently arising from formation of the unstable 2,3-dihydrotriphenylene, which undergoes loss of hydrogen.[94]

From the thermodynamic argument offered early in this chapter, it was believed that 9,10-diperfluoroalkenylphenanthrenes offered a chance to observe a reversible thermal 6π electrocyclization in a 1,3(*Z*),5-triene system. The thermodynamics seemed favorable and the potential for relatively unprecedented fluorine shifts nonexistent due to the greater strength of the C-F *versus* C-H bond. In this light, it was initially discouraging to observe such a complex mixture upon thermolysis of **40**.

Thermolysis of 9,10-bis(trifluoroethenyl)phenanthrene (**40**) led to formation of two primary products and two secondary products as illustrated in Figure 2-39. One of the primary thermal products, 1,2,2,3,3,4-hexafluoro-2,3-dihydrotriphenylene (**41**), was observed to be formed to no more than 15% in the reaction mixture over the temperatures examined. Contrary to expectations, thermolysis of purified **41** under identical conditions used for cyliization of the parent triene demonstrated that the cyclization was irreversible. The cyclized

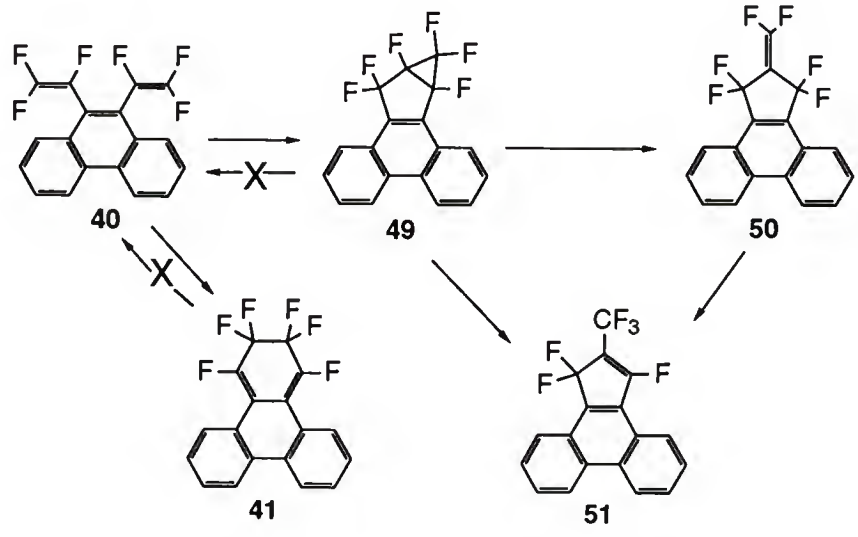


Figure 2-39. Transformations Observed Upon Thermolysis of 9,10-Bis(trifluoroethenyl)phenanthrene (**40**).

product **41** was predicted to be in an enthalpy range of 1 to -13 kcal/mol relative to the parent triene **40**. The fact that reversibility is not observed to any extent in this system leads to the conclusion that this process is occurring with $\Delta H_R \leq -5$ kcal/mol. A higher temperature study of this material was not undertaken as significant non-productive decomposition was found to be occurring at temperatures used to study **40**. As discussed earlier, having observed a good fit to first-order theory for the loss of **40** and a constant ratio of (**49+50+51**)/**41** over the individual runs examined, activation parameters of $\Delta H^{\ddagger} = 29.9 \pm 0.1$

kcal/mol and $\Delta S^{\ddagger}$ = -19.6 ± 0.3 cal/molxdeg were obtained for formation of **41** from **40**. Such parameters for the formation of **41**, being formally a 6π disrotatory process from **40**, are difficult to rationalize as no comparative kinetic data exists for cyclization of any other fluorinated 1,3(*Z*),5-triene system.

Formation of 1,4,4,5,6,6-hexafluoro-2,3-(9,10-phenanthro)bicyclo[3.1.0]-hex-2-ene (**49**) was observed to be the major process early in the reaction of **40**. This thermal cyclization of a fluorinated 1,3(*Z*),5-triene to form a fluorinated bicyclo[3.1.0]hex-2-ene is unprecedented in fluorocarbon literature and only one example, accompanied by minimal discussion, has been found in the corresponding hydrocarbon literature and is illustrated in Figure 2-40.[105] As

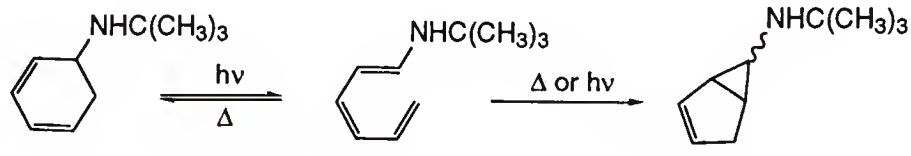


Figure 2-40. Thermal and Photoproducts of *E*-1-(*t*-Butylamino)-1,3(*Z*),5-hexatriene.

discussed earlier, the activation parameters obtained for formation of **49** from **40** are $\Delta H^{\ddagger}$ = 34.4 ± 2.8 kcal/mol and $\Delta S^{\ddagger}$ = -6.6 ± 6.0 cal/molxdeg. The unprecedented nature of this transformation does not allow for conjecture as to the mechanistic significance of these values. Thus, potential processes involved will be offered, with rationalization of the activation parameters left to the future.

The thermal closure of a 1,3(*Z*),5-triene system to a bicyclo[3.1.0]hex-2-ene ring is formally a Woodward and Hoffman allowed $4\pi_a + 2\pi_a$ or $4\pi_s + 2\pi_s$ process.[34] Determining the true stereochemical nature of the process requires at a minimum, labels at each terminus of the reacting 1,3,5-triene system. Due to the unprecedented nature of this thermal process, and the lack of

stereochemical labels in the aforementioned and **40** systems, the question of symmetry conservation can not begin to be addressed. The formation of **49** from **40** involves a further complication as the necessary primary intermediate **88** (Figure 2-41) has still to undergo a vinylcyclopropane-cyclopentene rearrangement to afford **49**. Figure 2-41 offers a representation of the potential processes involved in formation of **41** and **49**. Direct $4\pi_a + 2\pi_a$ or $4\pi_s + 2\pi_s$

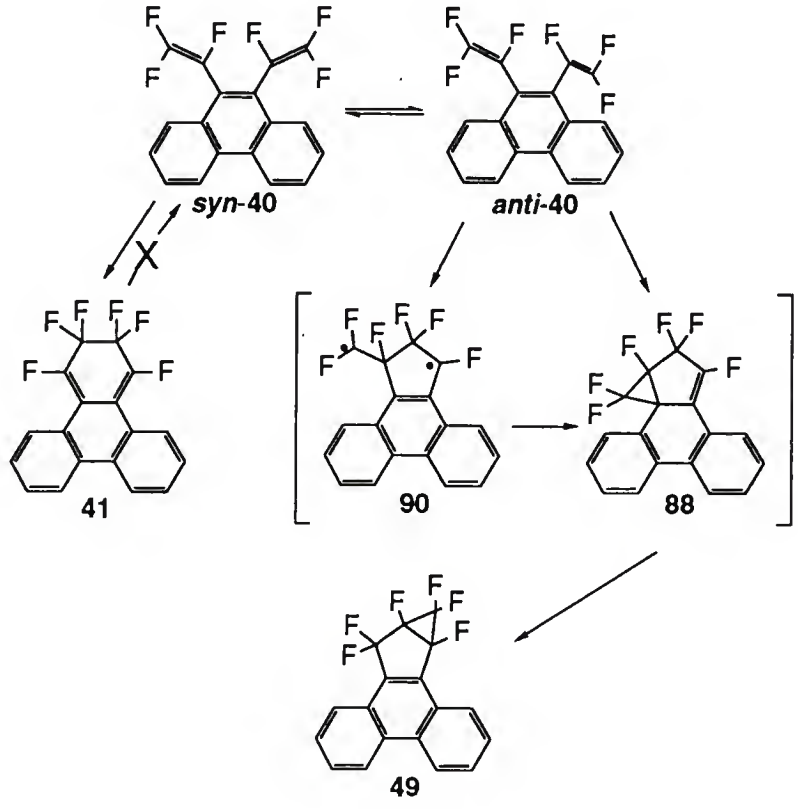


Figure 2-41. Mechanistic Rationale for Formation of **41** and **49**.

cyclization of ***anti*-40** could yield the primary intermediate **88**. As previously discussed, this material was also assumed to be a primary intermediate upon photolysis of **40**. Since this intermediate was not observed under the much lower temperature photolysis conditions, it would certainly not be observable under the thermolysis conditions. A vinylcyclopropane-cyclopentene

rearrangement must spontaneously occur as **88** is formed to relieve the strain in this spiro-fused system and restore aromaticity to the central phenanthrene ring. An alternate diradical process from ***anti*-40** may occur with formation of the intermediate **90**. In this case, closure of the terminus of one trifluoroethenyl substituent on the second at its carbon attached to the phenanthrene ring would yield the biradical **90** which may then recombine to **88** and rearrange to the observed product **49**.

1,4,4,5,6,6-Hexafluoro-2,3-(9,10-phenanthro)bicyclo[3.1.0]hex-2-ene (**49**) was observed to further rearrange under the thermolysis conditions to form **50** and **51** (Figure 2-39). Since **49** was unreactive with trace fluoride at lower temperatures and since disappearance of **49** follows first-order kinetics and yields linear Eyring plots over the temperatures and through the 70% extent of reaction examined, a mechanism involving fluoride catalysis can effectively be ruled out.

A hydrocarbon analog, bicyclo[3.1.0]hex-2-ene (**91**, Figure 2-42), is known to undergo thermal C1-C5 cyclopropane bond homolysis to yield biradical **92**, in which 1,2-H shifts may occur in two possible directions leading to the observed products 1,4- and 1,3-cyclohexadiene (**93**, **94**).[54]

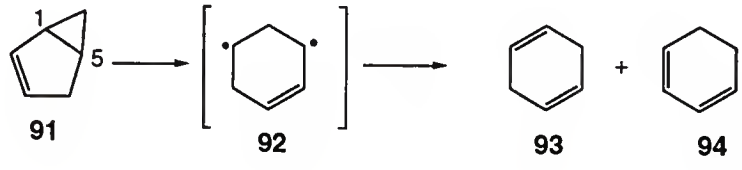


Figure 2-42. Thermolysis of Bicyclo[3.1.0]hex-2-ene (**91**).

Thermolysis of benzobicyclo[3.1.0]hex-2-ene (**95**, Figure 2-43) has been studied by the flash vacuum technique.[106] Over the high temperatures investigated (500-900°C), it was found that the major primary product was

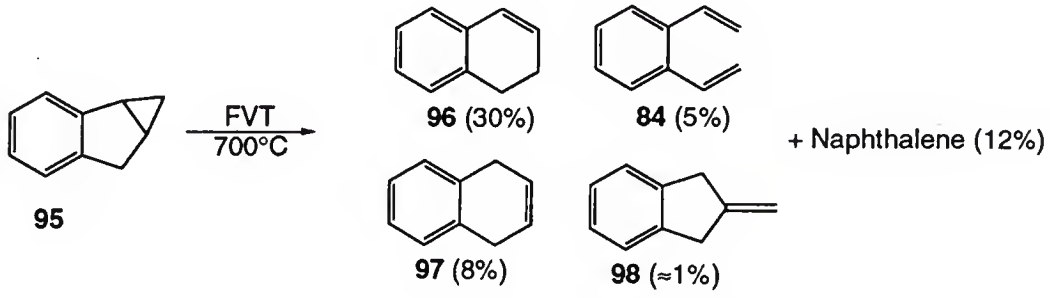


Figure 2-43. Flash Vacuum Thermolysis of Benzobicyclo[3.1.0]hex-2-ene (**95**).

1,2-dihydronaphthalene (**96**) with a variety of minor products (**84**, **97**, **98**) also observed. These products were proposed as arising from homolytic cleavage of the appropriate cyclopropane ring bond followed by a hydrogen shift (**96**, **97**, **98**) and electrocyclic process (**84**).

Gas and solution phase thermal rearrangement of perfluorobenzobicyclo[3.1.0]hex-2-ene (**100**, Figure 2-44) has been reported in a study addressing the reaction of perfluoroindene (**99**) with sources of difluorocarbene.[107,108] Perfluoroindene (**99**) was found to react with difluorocarbene generated from thermolysis of hexafluoropropylene oxide (HFPO). At lower temperatures, perfluorobenzobicyclo[3.1.0]hex-2-ene (**100**) was found to be the major product with smaller amounts of perfluorodihydronaphthalenes (**101**, **102**) and perfluoro-2-methylindene (**103**) also being observed. Thermolysis of **100** was also independently investigated. Thermolysis of neat **100** at 230°C yielded an 1:1:7 mixture of **99**:**102**:**103** and thermolysis at 670°C in a flow system yielded an 3:1 mixture of **99**:**103**.

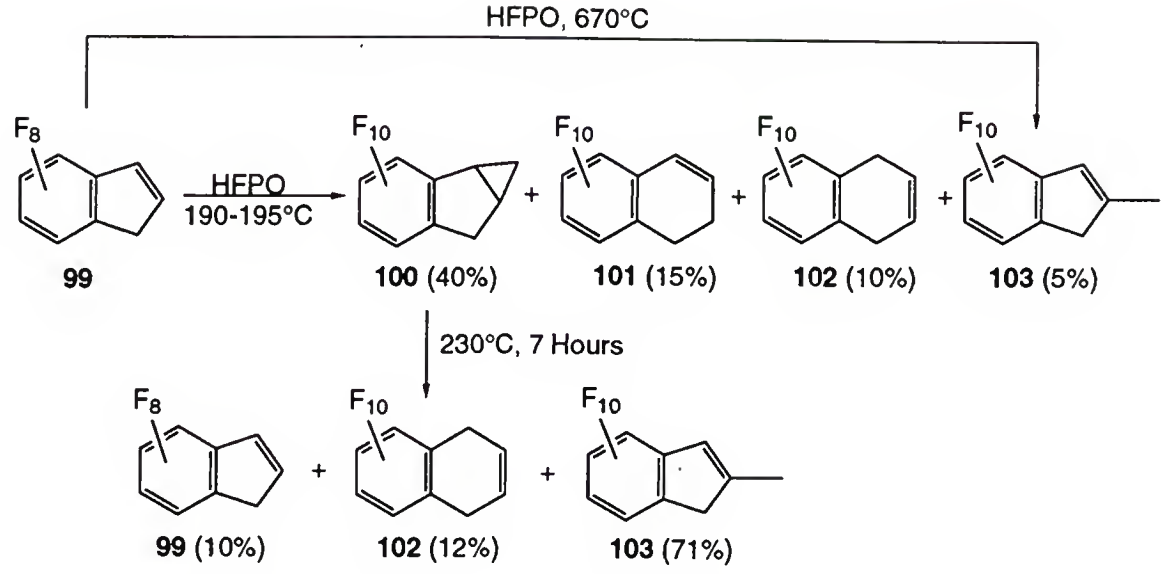


Figure 2-44. Reaction of Perfluoroindene (**99**) with Difluorocarbene and Thermolysis of Perfluorobenzobicyclo[3.1.0]hex-2-ene (**100**).

Elimination of difluorocarbene[6] can be a facile process in highly fluorinated cyclopropanes and was observed in the thermal study of perfluorobenzobicyclo[3.1.0]hex-2-ene (**100**), albeit at higher temperatures than were involved in our study of **49**. This process was revealed by formation of significant amounts of perfluoroindene **99** upon thermolysis of **100**. The analogous compound in the case of **49** was never observed in any of the thermolysis runs with **40** or **49**. On these grounds, a mechanism involving difluorocarbene can be ruled out.

Considering the above results, the observed thermal rearrangement of **49** to form **50** and **51** is not out of character. Figure 2-45 illustrates the possible mechanistic route involved. Homolytic cleavage of only one out of the three cyclopropane bonds in **49** is found to productively lead to products. Cleavage of bonds ***a*** (**104**) or ***b*** (**105**) leads to biradicals which in both cases

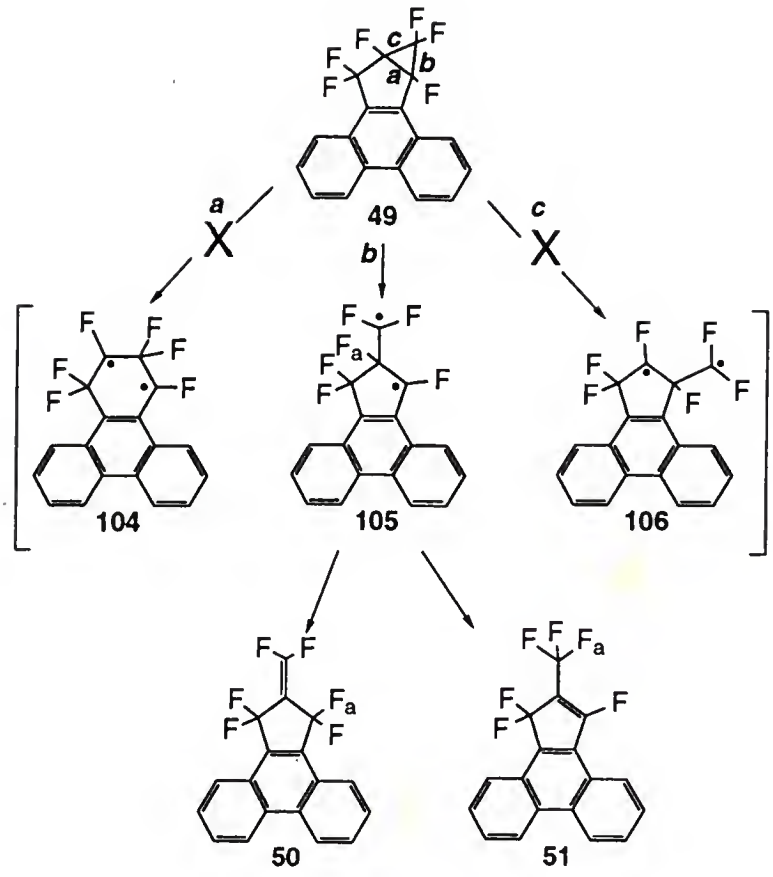


Figure 2-45. Mechanistic Rationale for Thermal Decomposition of 1,4,4,5,6,6-Hexafluoro-2,3-(9,10-phenanthro)bicyclo[3.1.0]hex-2-ene (**49**).

have one benzylic center; the other being on a secondary (**104**) and primary (**105**) carbon. Appreciable overlap with the C9-C10 phenanthrene π system early in cleavage of bond ***b*** may also facilitate such a process relative to cleavage of bond ***a*** or ***c***. Geminal difluorination of cyclopropanes is known to weaken the C-C bond opposite to the fluorinated site and those adjacent to the fluorinated site, although the weakening of the opposite bond is significantly greater.[6] Such an effect may be thought to possibly lead to facilitation of cleavage of bond ***a***. Here this factor is unlikely to be significant since this cyclopropane system also contains fluorine at sites β to the geminally difluorinated site which would counter such a disparity in bond strengths. The

final observed products require a 1,2-fluorine atom shift from the intermediate biradical. A 1,2-fluorine atom shift in the case of **104** will be a higher energy process than one in **105** due to the cleavage of the stronger C-F bond at the difluorinated site in the former. This fact together with the stereoelectronic preference for bond ***b*** cleavage and benzylic stabilization in **105** leads to observation of products arising only from cleavage of **49** to **105**. The other possible ring cleavage route ***c*** to form biradical **106** is disfavored as such a system affords no benzylic stabilization. The final observed products **50** and **51** then arise from 1,2-fluorine atom shifts of F_a (Figure 2-45) in one of two directions in **105**. The slightly favored product **50** is formed by shift towards the stabilized radical center.

Fluorine atom shifts lack unambigous precedent in the literature. Thermal [1,3] and [1,5]-fluorine atom shifts have been invoked in studies involving isomerizations of dihydrohexafluorocyclohexa-1,3-dienes[109] and perfluoroisoindenes.[110] Photochemical [1,5]-fluorine atom shifts have been invoked in the isomerization of perfluoroindene to perfluoroisoindene[111] and a rearrangement of perfluorotricyclo[5.2.2.$0^{2,6}$]undeca-2,5,8-triene (**107**) to perfluorotricyclo[5.2.2.$0^{2,6}$]undeca-2,3,8-triene (**108**).[88]

Figure 2-46. Photochemical [1,5]-Fluorine Atom Shift in Perfluorotricyclo-[5.2.2.$0^{2,6}$]undeca-2,5,8-triene (**107**).

Steric Effects in Thermal 1,3(*Z*),5-Triene Electrocyclizations

The rule of orbital symmetry conservation for a concerted process requires that C1-C6 bond formation in the thermal rearrangement of a 1,3(*Z*),5-triene to a 1,3-cyclohexadiene occur by overlap of π orbitals on the same side of the triene plane; hence defining a disrotatory process. A consequence of this type of process is that 1,3(*Z*),5-triene C1 and C6 *cis* substituents are forced into a more crowded position in the transition state than in the ground state. It is found that higher activation energies are required to bring C1 and C6 within bonding distance in the transition state due to this crowding, and often the energy of the 6π process will be sufficiently high so that alternate processes are observed to varying extents.

Activation parameters for a variety of systems in the literature demonstrate this steric effect and a few examples are given in Figure 2-47. Many of the examples found (**109**,[52] **110**,[52] **111**,[112] **112**[112]) show little change in activation entropy, indicating similar transition state geometry and timing is being maintained, therefore, the strain being built into the transition state is manifesting itself as a measurable increase in activation enthalpy. Sufficiently hindered systems (**113**[73]) often do not undergo 6π cyclization from the initial 1,3(*Z*),5-triene, but rearrange by other processes such as hydrogen shifts to trienes which are more suited for the disrotatory process.

An interesting result has been reported for the thermal study of 6π ring closure in a C1 and C6 deuterated *Z*-1,3,5-hexatriene (Figure 2-48).[113] Secondary isotope effects (k_H/k_D) of 1.05 for 1*E*,5*E*-D_2 (**114**) and 0.88 for 1*Z*,5*Z*-D_2 (**115**) were observed. The two transition states involved are diastereomerically related with respect to the deuterium substituents. Due to the different stereochemical environments in the transition state, an increase in

intramolecular non-bonding interactions was proposed to increase the force constants in the case of the terminally *cis*-deuterated material **115** and give rise to the inverse k_H/k_D effect observed .

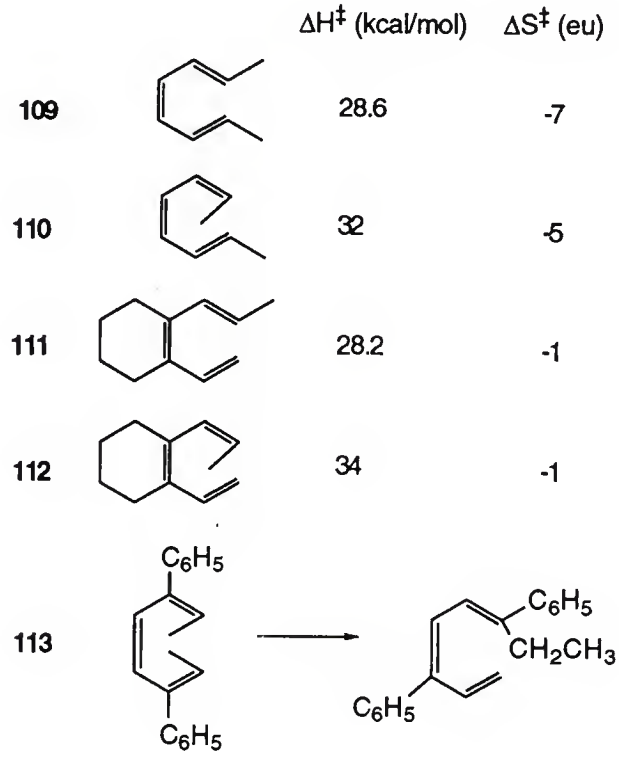
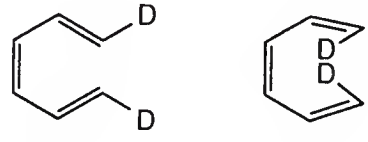


Figure 2-47. Activation Parameters for Non-Hindered *versus* Hindered 1,3(*Z*),5-Triene Cyclizations.



114 **115**

Figure 2-48. 1*E*,5*E*-D_2 (**114**) and 1*Z*,5*Z*-D_2-1,3(*Z*),5-Hexatriene (**115**).

1,3(*Z*),5-Triene cyclizations have received considerable theoretical interest. In calculated transition states for the disrotatory 6π 1,3(*Z*),5-triene electrocyclization, a definite steric crowding in is found between the C1 and C6

cis substituents.[72,113,114,115,116] The transition state is a boat-like ring conformation (Figure 2-49) with C1 and C6 *cis* hydrogens twisted in and separated by less than the sum of their van der Waal's radii.

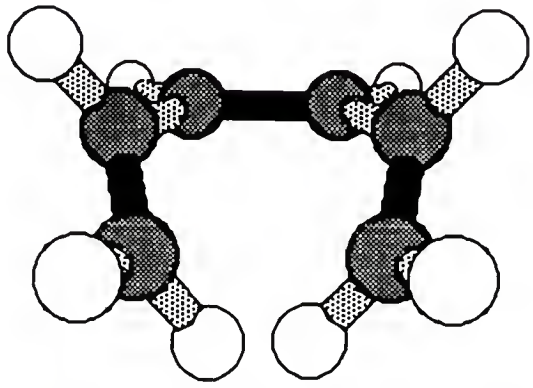


Figure 2-49. Approximate Representation of the Calculated 1,3(*Z*),5-Triene Disrotatory Transition State.

Conclusions

It is believed that for the cases of the fluorinated 1,3(*Z*),5-trienes examined in this study and found in the literature; 9,10-bis(trifluoroethenyl)phenanthrene (**40**), perfluoro-*E*,*Z*,*E*-4,5-dimethyl-2,4,6-octatriene (***Z*-56**), and perfluoro-*Z*-1,3,5-hexatriene (**76**), significant repulsion must develop between the C1 and C6 1,3(*Z*),5-triene *cis* fluorines upon approach to the boat-like disrotatory transition state. This repulsion leads to an increase in the energy barrier for this process and subsequently, increased potential for occurrence of competing processes. The observation of cyclobutene products from 4π conrotatory ring closure in these systems seems reasonable in light of this increased barrier. Closure in a 4π conrotatory manner is proposed to have a transition state which does not contain crowding of the terminal *cis* substituents as illustrated in Figure 2-50.[117,118] This together with the observed reversal of the relative thermodynamics in the perfluorinated

and hydrocarbon cyclobutene/1,3-diene systems lead to 4π closures as facile and primary processes in the thermolysis of fluorinated 1,3(*Z*),5-trienes.

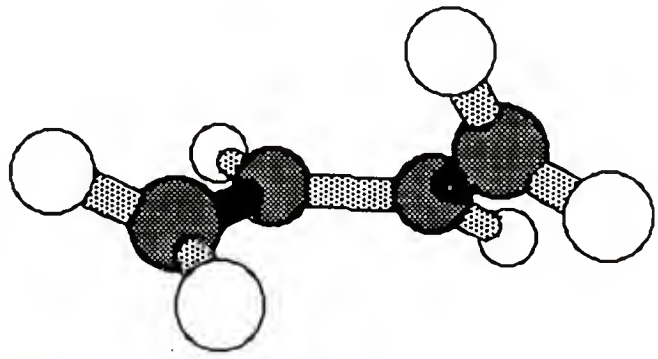


Figure 2-50. Approximate Representation of the Calculated 1,3-Diene Conrotatory Transition State.

An analogous process to the reported 6π thermal closure of perfluoro-*Z*-1,3,5-hexatriene at higher temperatures was never observed in thermal studies of perfluoro-*E*,*Z*,*E*-4,5-dimethyl-2,4,6-octatriene (***Z*-56**) most likely because sufficiently high temperatures were not used in the study of this material.

The fact that terminal *cis* fluorines impede the 1,3(*Z*),5-triene disrotatory process should not be surprising in light of the previous discussions. It is surprising though, in terms of the magnitude of the effect. The fact is that in these fluorinated systems, 4π cyclization is favored over 6π, and occurring roughly at temperatures necessary for the hydrocarbon 6π rearrangement. This large deviation in the thermal chemistry of fluorocarbon from hydrocarbon precedent upon terminal 1,3(*Z*),5-triene *cis* fluorination created the impetus for further study of fluorine's effect on thermal processes involving disrotatory and conrotatory transition states. Out of this interest, a strategy designed to provide more insight to this seeming steric influence of fluorine was developed and it's study is described in Chapter 3.

CHAPTER 3

[3,3]-SIGMATROPIC REARRANGEMENTS OF TERMINALLY FLUORINATED 1,5-DIENES

Introduction

The observation that 6π thermal disrotatory closure of perfluorinated 1,3(*Z*),5-trienes is disfavored to such an extent that other primary processes occur exclusively, is unprecedented and encouraged further attention. The usual strong electronic influence of fluorine on a reaction process seemed in the disrotatory process to be offset by an factor more steric in origin. As discussed in Chapter 1, such influences are rarely responsible for the course of reaction in fluorinated organic systems due to the small difference between fluorine and hydrogen in size and bond length to carbon. Nevertheless, the tightly bound nature of the concerted transition state which is required for 1,3(*Z*),5-triene disrotatory cyclization leads to a twisting in and crowding of the terminal *cis* substituents which is believed to be at least partially responsible for the observed deviation of perfluorocarbon chemistry from that of analogous hydrocarbons. While precedent from the hydrocarbon literature indicated destabilization of such a transition state by groups substantially larger than hydrogen at the 1,3(*Z*),5-triene terminal *cis* positions, it seemed surprising that upon substitution of hydrogen by fluorine at these positions, rather than observing an higher energy disrotatory process, alternate rearrangements were observed. It was then the intention to study another system with a lesser degree of fluorination rearranging from a specific conformation which would allow a

more quantitative understanding of the effect terminal fluorination has on pericyclic processes.

The [3,3]-Sigmatropic Shift of 1,5-Dienes: The Cope Rearrangement

A hydrocarbon system which has been thoroughly scrutinized experimentally and theoretically is the Cope Rearrangement. This process is formally a subset of the family of sigmatropic shifts, which involve migration of a σ bonded atom or π system from one terminus of a conjugated π system to the other in a concerted fashion. The all carbon [3,3]-sigmatropic shift was discovered by Hurd[119] and later by Cope[120] and the most simple case involving the degenerate rearrangement of 1,5-hexadiene is illustrated in Figure 3-1.

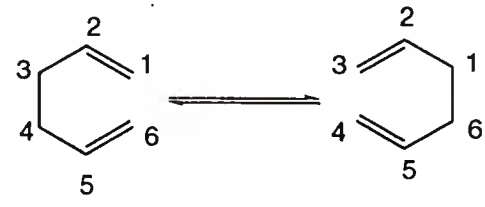


Figure 3-1. The Cope Rearrangement of 1,5-Hexadiene.

Orbital symmetry considerations dictate that the process occur in a [3_s,3_s] fashion, meaning that bonding occurs from the same face at the terminus of each three carbon fragment.[34] Such a restriction still allows for the rearrangement to occur through a number of viable conformations of the 1,5-diene system. Among the conformations available to this system, it has been experimentally demonstrated that the Cope rearrangement occurs preferentially through a chair conformation transition state except in cases where the system is geometrically constrained so as to make the chair inaccessible. A variety of studies involving stereochemically labeled 1,5-diene systems have

demonstrated the exclusive nature of this process and estimate the chair is favored over a boat conformation transition state by at least 6 kcal/mol in enthalpy.[54] Semiempirical[121] and more recent *ab initio*[122,123] level theoretical studies confirm by similar barriers the experimental preference found for the chair over the boat transition state conformation. The energy difference and hence the exclusive chair transition state for this process is rationalized as being due to a through space, destabilizing antibonding interaction between orbitals on C2 and C5 in the boat conformation.[34,124] Although there is no question as to the preferred conformation of the transition state, the aspect of synchronicity or bond timing in this concerted process has been under continuous debate. Such mechanistic finepoints will be addressed later in discussion but at this point, only the aspect of favored conformation will be considered.

The Cope system appears to be ideal for study of the effect of terminal fluorination, as the transition state geometries (Figure 3-2) contain the same bulk structural features which were rationalized as influencing the fluorinated thermal electrocyclic processes discussed in Chapter 2. The calculated transition state conformation for the thermal 6π disrotatory process[113] is structurally similar to a boat Cope process[121,122] and the photochemical 6π conrotatory process[125] is similar to the chair Cope process.[121,122] The Cope system surpasses the electrocyclic process in terms of utility for thermal study in that both the boat and chair Cope processes are orbital symmetry allowed thermal processes, whereas the electrocyclic disrotatory and conrotatory processes are allowed only for thermal and photochemical excitation respectively. The fundamental differences between the ground and excited state processes in the 6π electrocyclic study do not allow for easy comparison of activation parameters or discussion of steric and electronic effects of terminal

substituents between the two conformations. Seeing as both conformations may undergo symmetry allowed thermal Cope processes, design of appropriate terminally fluorinated 1,5-dienes and measurement of the activation parameters for Cope rearrangement would allow for a more quantitative understanding as to the effect of terminal fluorination on these transition state conformations.

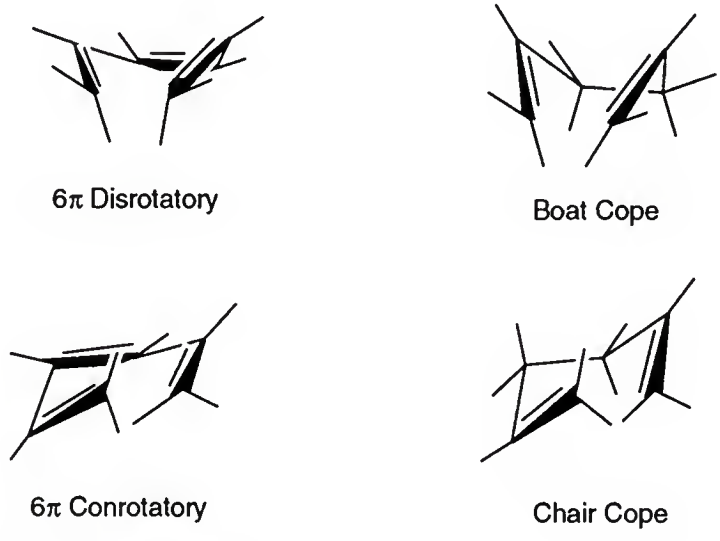


Figure 3-2. 6π Electrocyclic and Cope Transition State Conformations.

Fluorinated Cope Systems

The thermal study of fluorinated 1,5-dienes has received little qualitative or quantitative attention. Two recent reviews offer the minimal literature available addressing qualitative aspects of [3,3]-sigmatropic processes in fluorinated 1,5-dienes,[126] allylvinyl ethers,[126] and carbanions.[127]

The observation of the effect of terminal fluorine on a chair constrained thermal Cope process was most easily studied by synthesizing terminally fluorinated dienes which would complement hydrocarbon systems for which reliable activation parameters had been previously reported. Due to the degeneracy in the system, the parent 1,5-hexadiene had been studied as

1,1-dideutereo-1,5-hexadiene (Figure 3-3, **116**).[128] The partially fluorinated *E*- and *Z*-1-fluoro-1,5-hexadiene[129] (**118**, **119**), and 1,1-difluoro-1,5-hexadiene[129] (**121**) thermal studies had already been reported in the literature with reliable activation parameters. To complete the simple 1,5-hexadiene series required synthesis and thermal study of 1,1,6,6-tetrafluoro-1,5-hexadiene (**123**).

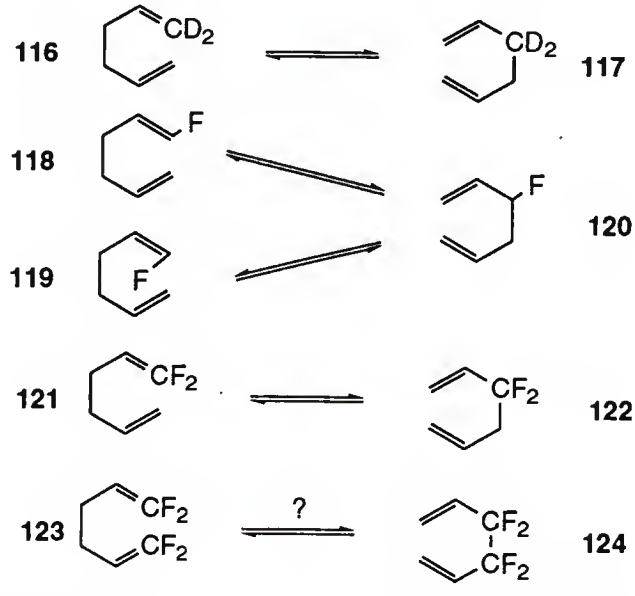


Figure 3-3. Fluorinated 1,5-Hexadiene Cope Processes of Interest.

The experimental study of boat constrained Cope systems has received a variety of interest, and again, systems were chosen for mechanistic novelty, activation parameter reliability of the reported hydrocarbons, and synthetic simplicity. Two hydrocarbon systems (Figure 3-4) which have been investigated where geometrical constraints force a boat conformation Cope rearrangement are 1,4-dimethylenecyclohexanes[130,131] such as **125**, and *meso*-1-(2-methylidenecyclopentyl)-2-methylidenecyclopentane[132] (***meso*-126**). An artifact of the synthetic route into ***meso*-126**, the *d,l*-1-(2-methylidene-cyclopentyl)-2-methylidenecyclopentane isomer ***d,l*-126** is also afforded. This

diastereomer is constrained to undergo the Cope rearrangement through a chair conformation, creating another system for comparison with those of Figure 3-3.

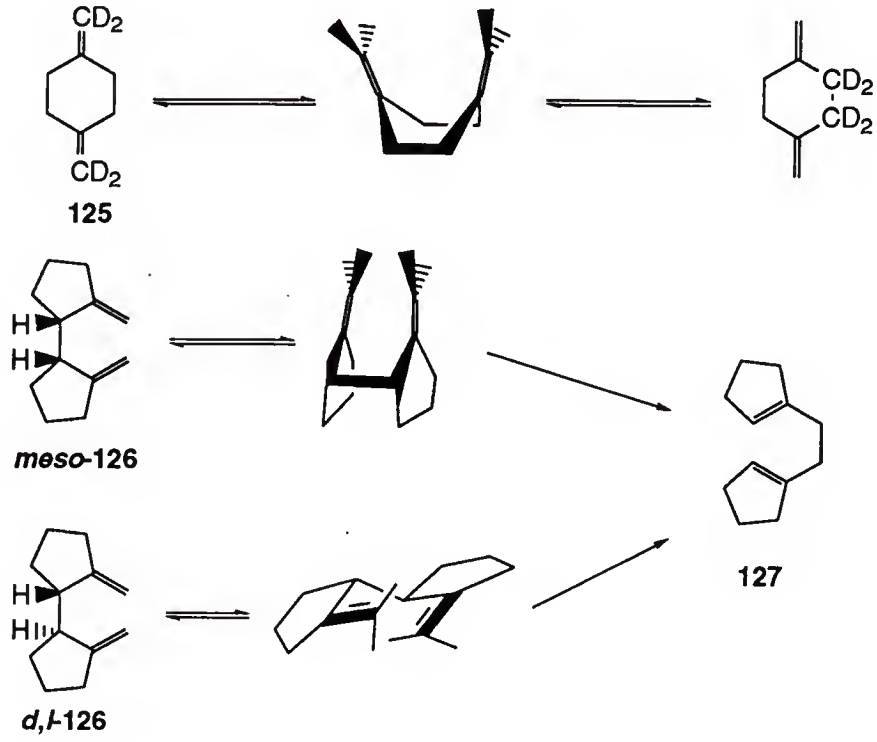


Figure 3-4. Cope Rearrangements in Conformationally Constrained Systems.

There is a subtle but important difference between the two boat conformations involved with **125** and ***meso*-126**. Due to the symmetry of the system, the boat type transition state for **125** will constrain the two terminal methylenes to approach one another in a coplanar eclipsed fashion with no twisting in of terminal substituents. In contrast, the *meso*-bismethylenecyclopentane ***meso*-126** will be able to accommodate a true boat transition state which involves a significant turning in of the two terminal *cis* substituents. A thermal study of 1,4-dideuteriomethylidenecyclohexane (**125**) has been reported as has a study of the hydrocarbon *d,l*- and

meso-bismethylenecyclopentanes (***d,l*-126**, ***meso*-126**), and all are reported with reliable activation parameters.

The materials then of interest in this study are illustrated in Figure 3-5. To probe the effect of terminal fluorination in these different systems, the synthesis of a variety of materials was required to complete each series from hydrocarbon, to terminally *gem*-difluorinated, to terminally bis-*gem*-difluorinated 1,5-diene. Having reliable reported activation parameters for **116**, **121**, **125**, and ***meso*** and ***d,l*-126**, it was necessary to carry out syntheses and thermal studies of **123**, **128**, **129**, ***meso*** and ***d,l*-130**, and ***meso*** and ***d,l*-131**. Although interest existed in ***meso*** and ***d,l*-130**, this system was not studied due to time limitations. The synthetic routes and thermal results for **123**, **128**, **129**, and ***meso*** and ***d,l*-131** will now be discussed.

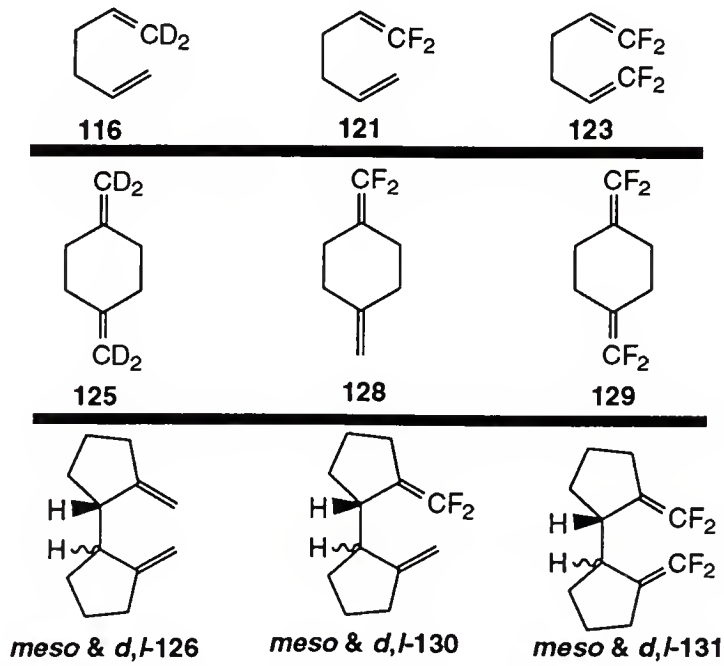


Figure 3-5. Three Hydrocarbon to Terminally Fluorinated 1,5-Diene Series.

Synthesis and Thermolysis of Terminally *Gem*-difluorinated 1,5-Diene Systems

1,1,6,6-Tetrafluoro-1,5-hexadiene (**123**)

1,1,6,6-Tetrafluoro-1,5-hexadiene (**123**) was synthesized in six steps from 1,4-butanediol in an overall isolated yield of 6%. The reaction sequence is illustrated in Figure 3-6. 4-[(Tetrahydro-2*H*-pyran-2-yl)oxy]-1-butanal (**132**) was prepared by a literature procedure[133] from 1,4-butanediol in two steps and subjected to a Wittig-type fluoroolefination[134] to yield 5-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1,1-difluoropent-1-ene (**133**). Deprotection to 5,5-difluoro-4-penten-1-ol (**134**) and pyridinium dichromate (PDC) oxidation yielded 5,5-difluoro-4-pentenal (**135**). Wittig-type fluoroolefination then afforded the desired 1,1,6,6-tetrafluoro-1,5-hexadiene (**123**). Initial attempts to obtain **123** through Wittig-type fluoroolefination of 1,4-butanedial did not afford any amount of fluoroolefin and was not further pursued.

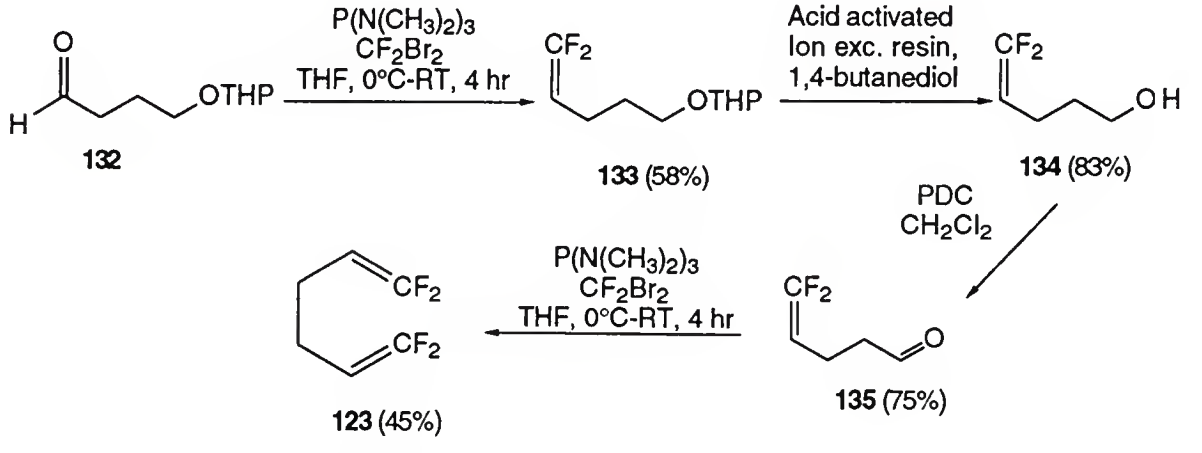
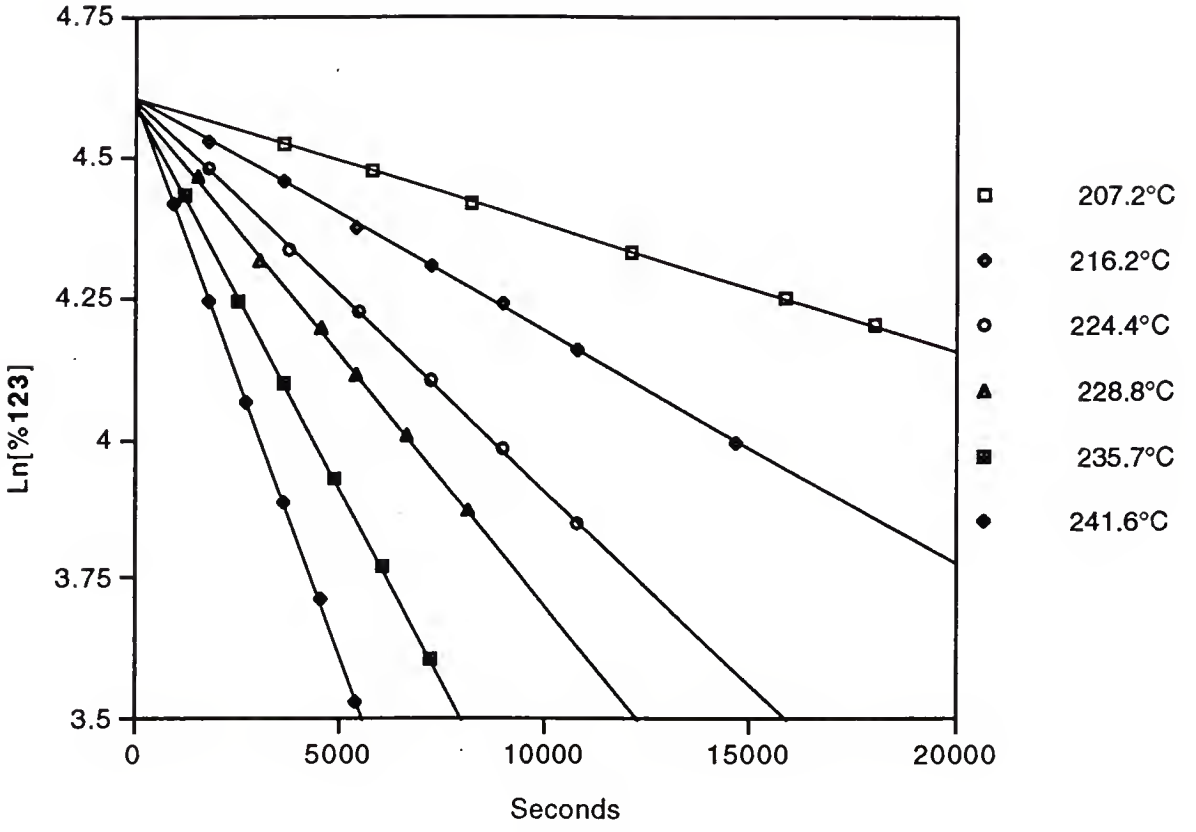


Figure 3-6. Synthesis of 1,1,6,6-Tetrafluoro-1,5-hexadiene (**123**).

Due to appreciable volatility, the thermolysis of **123** was examined in the gas phase as described in Appendix A. Quantitative conversion of **123** to



Temperature (°C)	k ($x10^5$ sec^{-1})	R^2
207.2	2.24 ± 0.01	0.9999
216.2	4.13 ± 0.05	0.9993
224.4	6.88 ± 0.07	0.9996
228.8	8.87 ± 0.12	0.9993
235.7	13.68 ± 0.07	0.9999
241.6	19.76 ± 0.10	0.9999

123 **124**

Figure 3-7. First-Order Rate Plots and Rate Constants for Thermolysis of 1,1,6,6-Tetrafluoro-1,5-hexadiene (**123**).

3,3,4,4-tetrafluoro-1,5-hexadiene (**124**, Figure 3-7) was observed. The thermolysis was examined at six temperatures from 207.2°C to 241.6°C and the conversion was observed to follow first-order kinetics with no degree of reversibility observed. Figure 3-7 offers the first-order plots and rate constants for the temperatures examined.

The activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$) for the cyclization were obtained using the Eyring expression,[68] $k = \frac{kT}{h} e^{\left(-\frac{\Delta H^{\ddagger}}{RT}\right)} e^{\left(\frac{\Delta S^{\ddagger}}{R}\right)}$, rearranged to the form $\ln(k/T) = -\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R + \ln(k/h)$, where k = rate constant at absolute temperature T, ***k*** = Boltzmann constant (1.381×10^{-23} J/K), ***h*** = Planck's constant (6.626×10^{-34} Jxs), and R = ideal gas constant (1.9872 cal/molxK). A linear least-squares regression plot of Ln(k/T)*versus* 1/T, as illustrated in Figure 3-8, yielded $\Delta H^{\ddagger}$ = 29.9 ± 0.2 kcal/mol and $\Delta S^{\ddagger}$ = -18.5 ± 0.5 cal/molxdeg for the Cope rearrangement of **123** to **124** with the errors reported as one standard deviation.

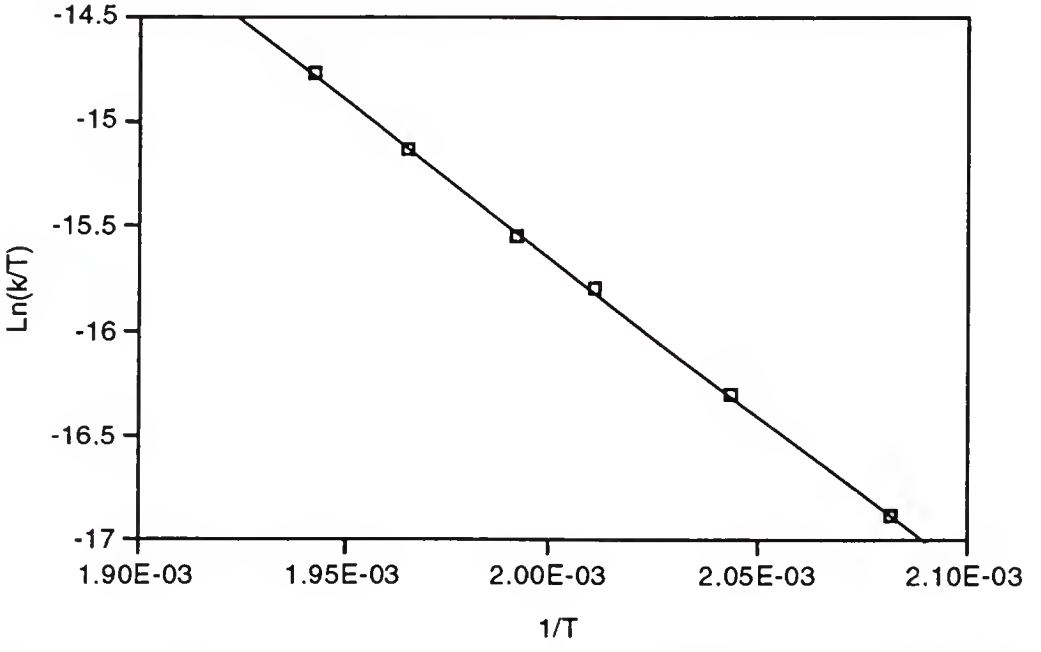


Figure 3-8. Eyring Plot for Thermolysis of 1,1,6,6-Tetrafluoro-1,5-hexadiene (**123**).

1-Difluoromethylidene-4-methylidenecyclohexane (**128**)

1-Difluoromethylidene-4-methylidenecyclohexane (**128**) was prepared in three steps from 1,4-cyclohexanedione mono-ethylene ketal (**136**) in a 37% isolated yield. The reaction sequence is illustrated in Figure 3-9.

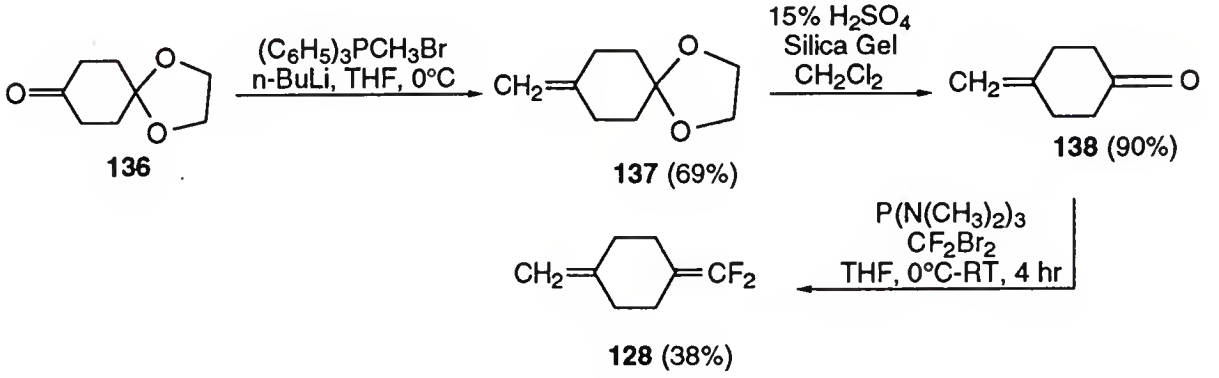
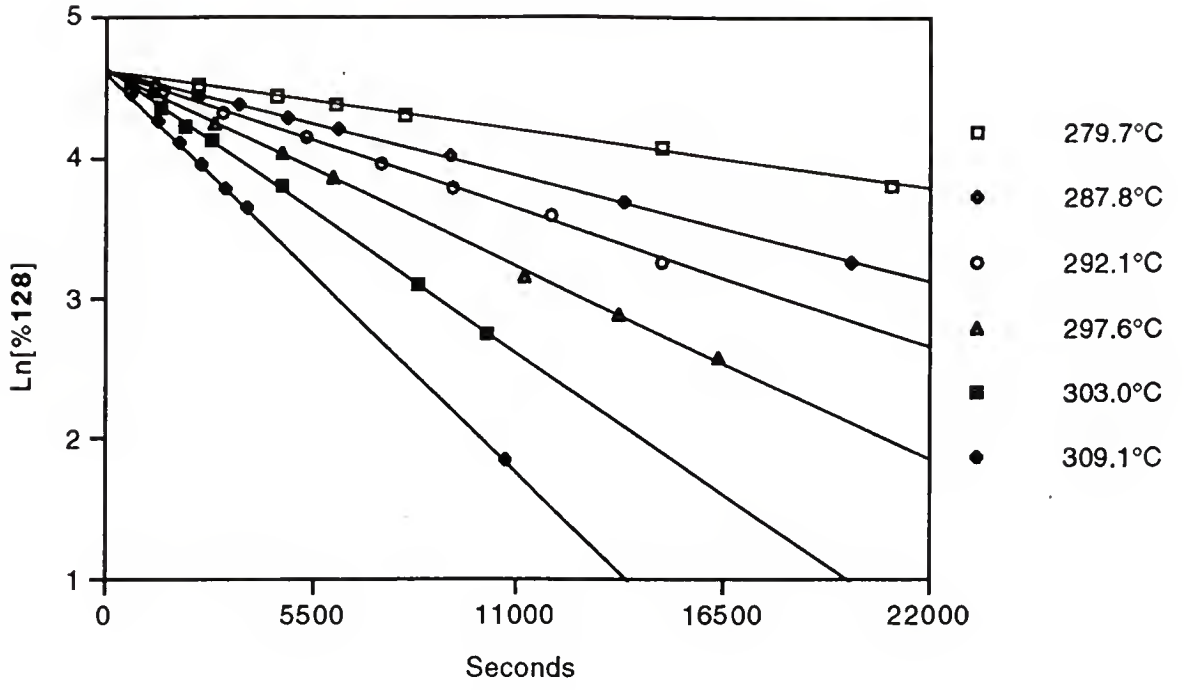


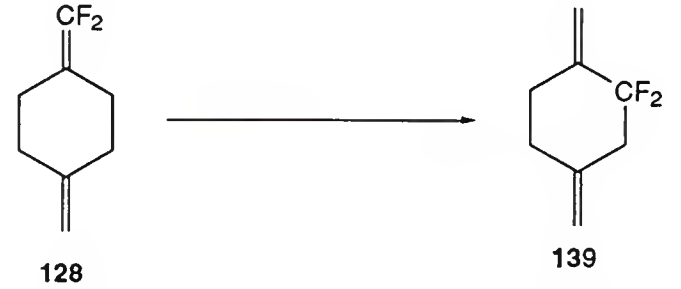
Figure 3-9. Synthesis of 1-Difluoromethylidene-4-methylidenecyclohexane (**128**).

4-Methylidene-1-cyclohexanone ethylene ketal (**137**) was prepared from 1,4-cyclohexanedione mono-ethylene ketal (**136**) by a Wittig reaction[135] then deprotected[136] to yield 4-methylidenecyclohexanone (**138**). This material was subjected to Wittig-type fluoroolefination[134] to yield the desired **128**.

Due to appreciable volatility, the thermolysis of **128** was examined in the gas phase as described in Appendix A. Quantitative conversion of **128** to 1,1-difluoro-2,5-dimethylidenecyclohexane (**139**, Figure 3-10) was observed. The thermolysis was examined at six temperatures from 279.9°C to 309.1°C. The conversion was observed to follow first-order kinetics and no degree of reversibility was observed. Figure 3-10 offers the first-order plots and rate constants for the temperatures examined.



Temperature (°C)	k ($x10^5$ sec^{-1})	R^2
279.9	3.78 ± 0.09	0.9976
287.8	6.72 ± 0.04	0.9998
292.1	8.88 ± 0.19	0.9977
297.6	12.51 ± 0.19	0.9989
303.0	18.12 ± 0.15	0.9996
309.1	25.72 ± 0.16	0.9998



128 **139**

Figure 3-10. First-Order Plots and Rate Constants for Thermolysis of 1-Difluoromethylidene-4-methylidenecyclohexane (**128**).

A linear regression plot of Ln(k/T)*versus* 1/T (Figure 3-11), as described in the case of **123**, yielded $\Delta H^{\ddagger}$ = 40.8 ± 0.5 kcal/mol and $\Delta S^{\ddagger}$ = -6.1 ± 0.9 cal/molxdeg for the Cope rearrangement of **128** to **139**.

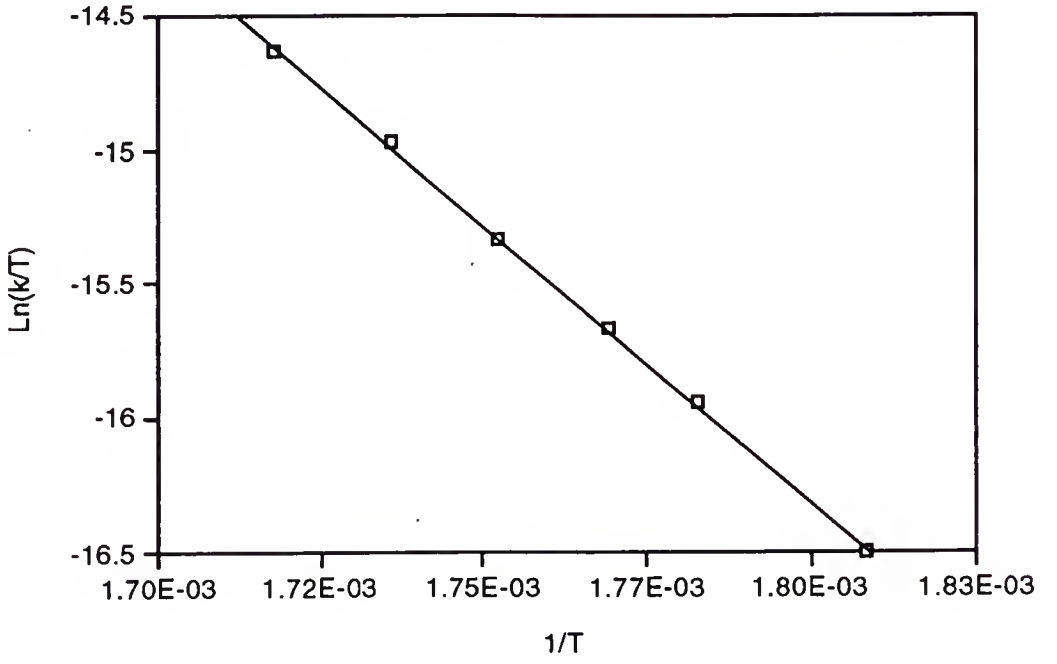
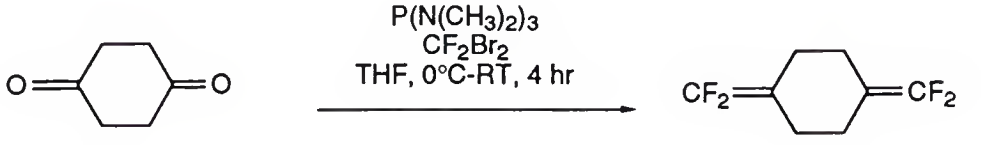


Figure 3-11. Eyring Plot for Thermolysis of 1-Difluoromethylidene-4-methylidenecyclohexane (**128**).

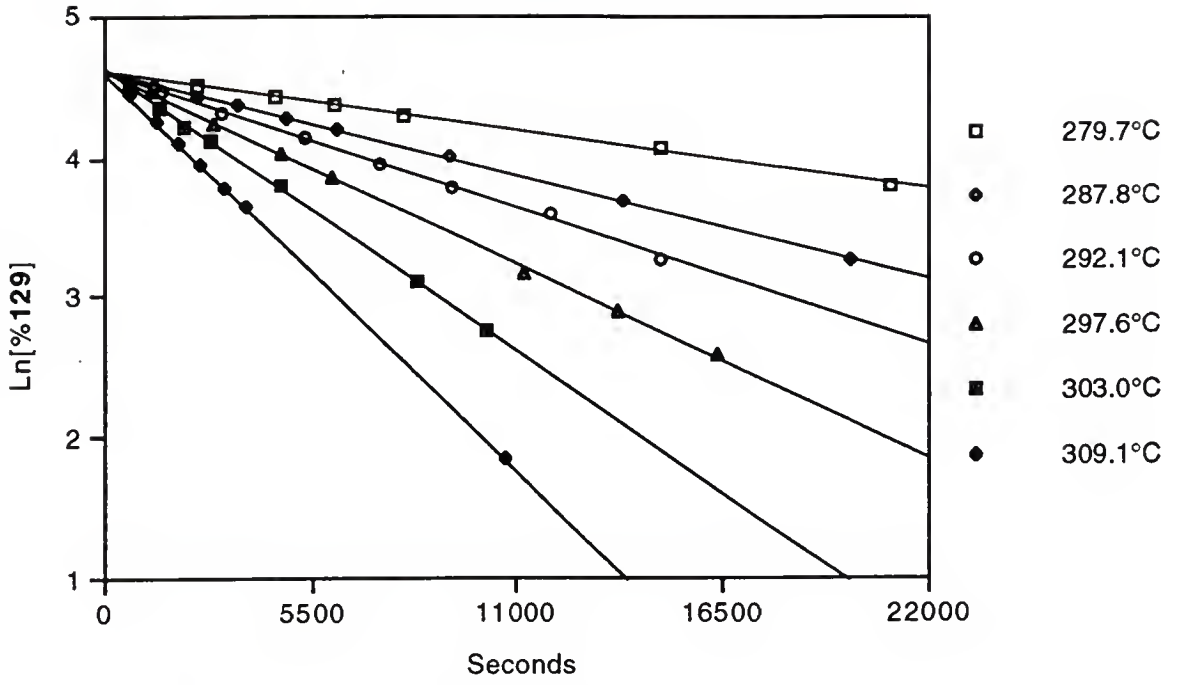
1,4-Di(difluoromethylidene)cyclohexane (**129**)

1,4-Di(difluoromethylidene)cyclohexane (**129**) was synthesized in one step (Figure 3-12) from 1,4-cyclohexanedione (**140**) by a Wittig-type fluoroolefination[134] and isolated in an 36% yield.

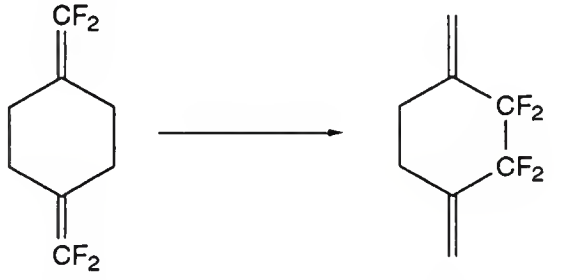


140 **129** (36%)

Figure 3-12. Synthesis of 1,4-Di(difluoromethylidene)cyclohexane (**129**).



Temperature (°C)	k (x10⁴ sec⁻¹)	R^2
329.2	1.35 ± 0.02	0.9993
336.9	2.07 ± 0.05	0.9980
343.2	3.00 ± 0.02	0.9998
349.1	4.02 ± 0.10	0.9980
354.5	5.47 ± 0.15	0.9968
359.8	7.40 ± 0.11	0.9993



129 **141**

Figure 3-11. First-Order Plots and Rate Constants for Thermolysis of 1,4-Di(difluoromethylidene)cyclohexane (**129**).

Due to appreciable volatility, the thermolysis of **129** was examined in the gas phase as described in Appendix A. Quantitative conversion of **129** to 1,1,2,2-tetrafluoro-3,6-dimethylidenecyclohexane (**141**, Figure 3-13) was observed. The thermolysis was examined at six temperatures from 329.2°C to 359.8°C. The conversion was observed to follow first-order kinetics and no degree of reversibility was observed. Figure 3-13 shows the first-order plots and rate constants for the temperatures examined.

A linear regression plot of Ln(k/T)*versus* 1/T, as described in the case of **123**, yielded $\Delta H^{\ddagger}$ = 40.7 ± 0.5 kcal/mol and $\Delta S^{\ddagger}$ = -10.1 ± 0.8 cal/molxdeg for the Cope rearrangement of **129** to **141**.

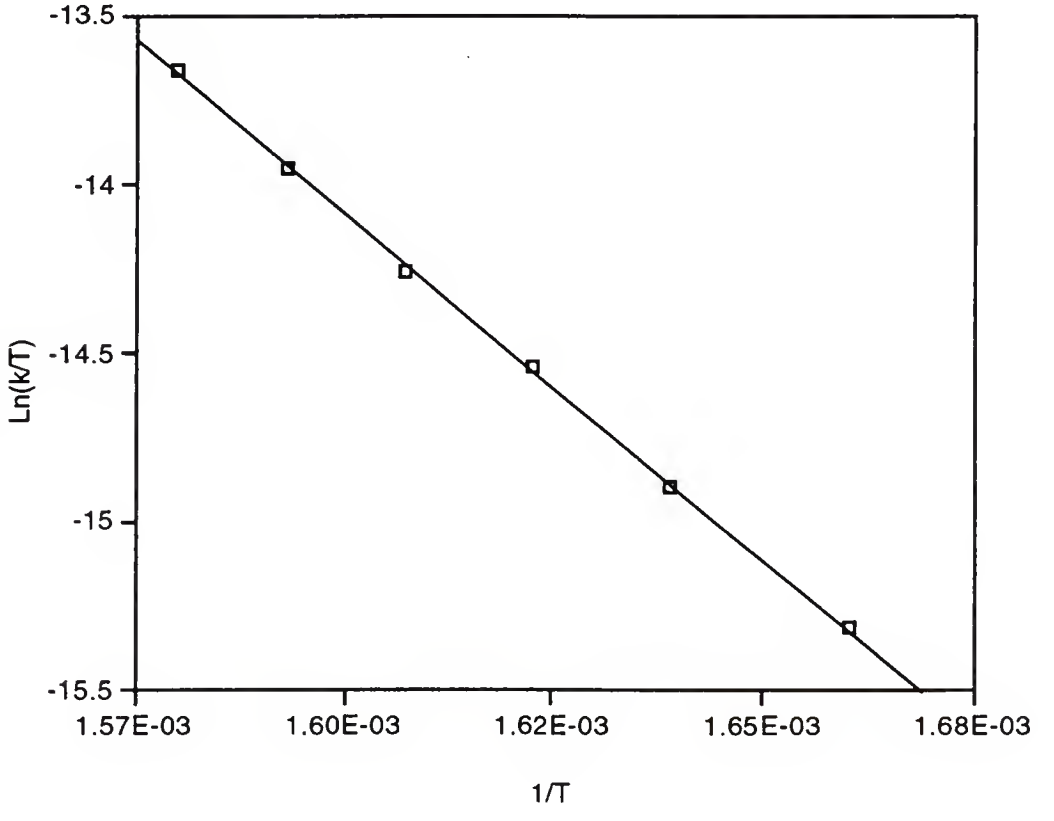


Figure 3-14. Eyring Plot for Thermolysis of 1,4-Di(difluoromethylidene)-cyclohexane (**129**).

meso- and *d,l*-1-(2-Difluoromethylidenecyclopentyl)-2-difluoromethylidene-cyclopentane (***meso*-131**,***d,l*-131**)

***Meso*-131** and ***d,l*-131** were prepared in four steps and isolated in 7% overall yield as illustrated in Figure 3-15. 2-Chlorocyclopentanone was added to the sodium enolate of ethyl 2-oxocyclopentanecarboxylate (**142**), and the resultant material decarboxylated under acid catalysis to yield 2-(2-oxocyclopentyl)cyclopentanone (**143**).[137] This material was subjected to Wittig-type fluoroolefination[134] to yield 1-(2-difluoromethylidenecyclopentyl)-2-difluoromethylidenecyclopentane (**131**) in a 5.41:1 ratio of *d,l* to *meso*. Due to

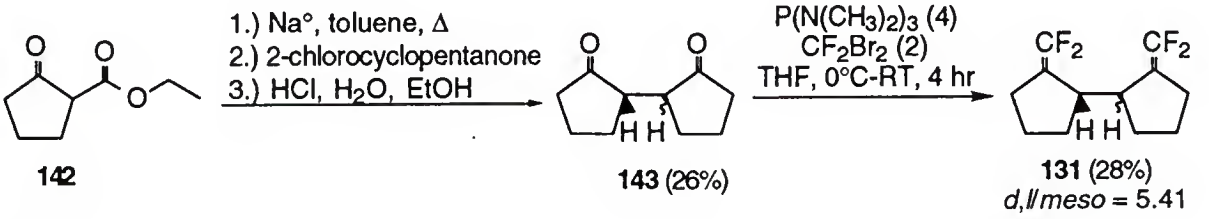


Figure 3-15. Synthesis of *meso*- and *d,l*-1-(2-Difluoromethylidenecyclopentyl)-2-difluoromethylidenecyclopentane (***meso*-131**,***d,l*-131**).

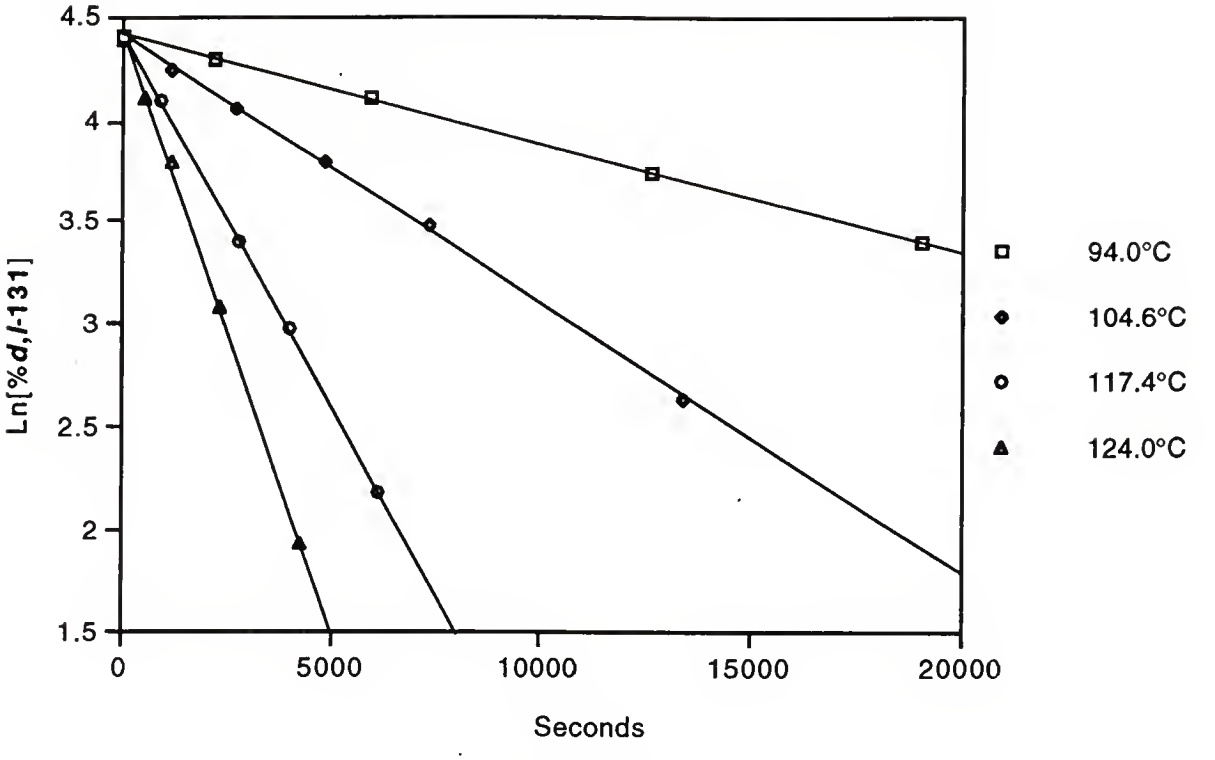
insufficient vapor pressure at the operating conditions of the gas kinetics line and problems with condensation of the material on cool line sections and joints, it was necessary to study the thermolysis of **131** in solution. A 0.54 M solution of **131** was prepared in *n*-dodecane and the extent of conversion was followed *versus* internal standard by ^{19}F NMR. The temperatures necessary to afford the rearrangement of ***meso*-131** were roughly 200°C higher than those required for rearrangement of ***d,l*-131**. This allowed the mixture of diastereomers to be thermolyzed and kinetics observed independently. Disappearance of the *d,l* material was studied first at a lower temperature, followed by higher temperature study of the rearrangement of the *meso* material, thus enabling two rate constants to be obtained from one sample. Due to difficulties with the

apparatus and time involved for the quantitative NMR observations, a limited number of temperatures were utilized for these systems. Quantitative conversion of ***d,l*-131** to 1-(2-(1-cyclopentenyl)-1,1,2,2-tetrafluoroethyl)-cyclopentene (**144**, Figure 3-16) was observed. The thermolysis of ***d,l*-130** was examined at four temperatures from 94.0°C to 124.0°C. Transformation of ***meso*-131** to **143** was observed at three temperatures from 274.4°C to 293.1°C. Small amounts (<10%) of unidentified materials were observed by ^{19}F NMR after longer periods of time at these elevated temperatures. Conversions of both ***d,l*-131** and ***meso*-131** were observed to follow first-order kinetics and no extent of reversibility was observed. Figures 3-16 (***d,l*-131**) and 3-17 (***meso*-131**) show the first-order plots and rate constants for the temperatures examined.

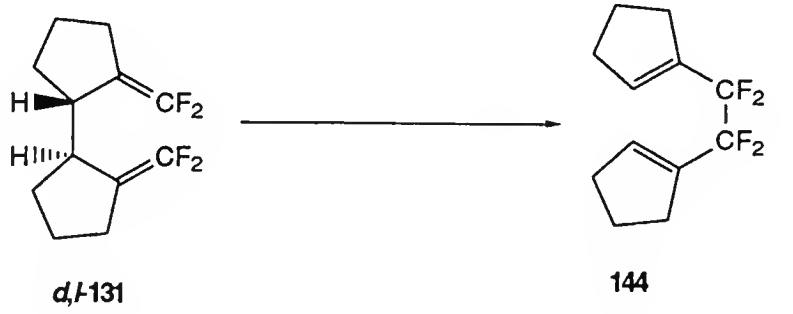
Linear regression plots of Ln(k/T)*versus* 1/T, as described in the case of **123**, yielded $\Delta H^{\ddagger}$ = 22.4 ± 0.2 kcal/mol and $\Delta S^{\ddagger}$ = -17.5 ± 0.4 cal/mol deg for the Cope rearrangement of ***d,l*-131** to **144** (Figure 3-19) and $\Delta H^{\ddagger}$ = 49.5 ± 1.0 kcal/mol and $\Delta S^{\ddagger}$ = 8.1 ± 1.7 cal/molxdeg for the rearrangement of ***meso*-131** to **144** (Figure 3-20).

Discussion

Increasing the degree of terminal *gem*-difluorination in a 1,5-diene system was found to have a small but significant influence on the Cope processes occurring through chair transition states and a variable influence on those occurring through boat constrained geometry. Figure 3-21 offers activation parameters for hydrocarbon and terminally fluorinated systems from this study and the literature undergoing chair transition state Cope rearrangements. No significant influence is observed upon terminal

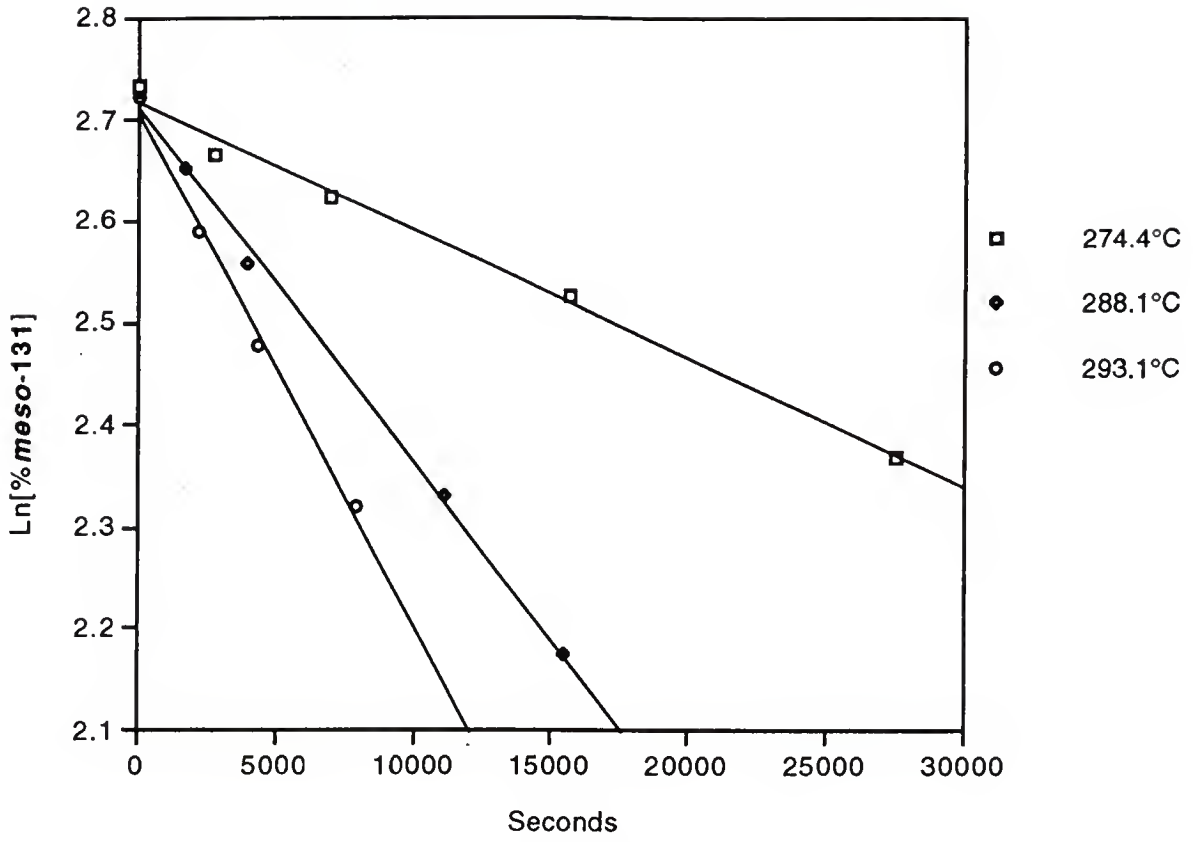


Temperature (°C)	k (x10^5 sec^{-1})	R^2
94.0	5.32 ± 0.06	0.9995
104.6	13.09 ± 0.13	0.9996
117.4	36.27 ± 0.33	0.9997
124.0	57.98 ± 1.01	0.9991

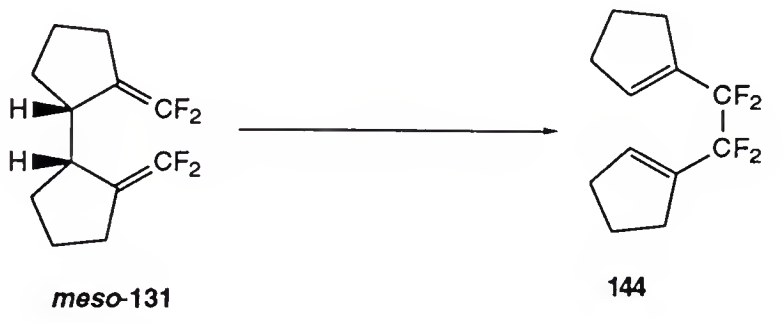


d,l-131 144

Figure 3-16. First-Order Plots and Rate Constants for Thermolysis of *d,l*-1-(2-Difluoromethylidenecyclopentyl)-2-difluoromethylidenecyclopentane (***d,l*-131**).



Temperature (°C)	k ($\times 10^5$ sec^{-1})	R^2
274.4	1.09 ± 0.07	0.9904
288.1	3.47 ± 0.11	0.9969
293.1	5.03 ± 0.32	0.9919



meso-131 144

Figure 3-17. First-Order Plots and Rate Constants for Thermolysis of *meso*-1-(2-Difluoromethylidenecyclopentyl)-2-difluoromethylidenecyclopentane (***meso*-131**).

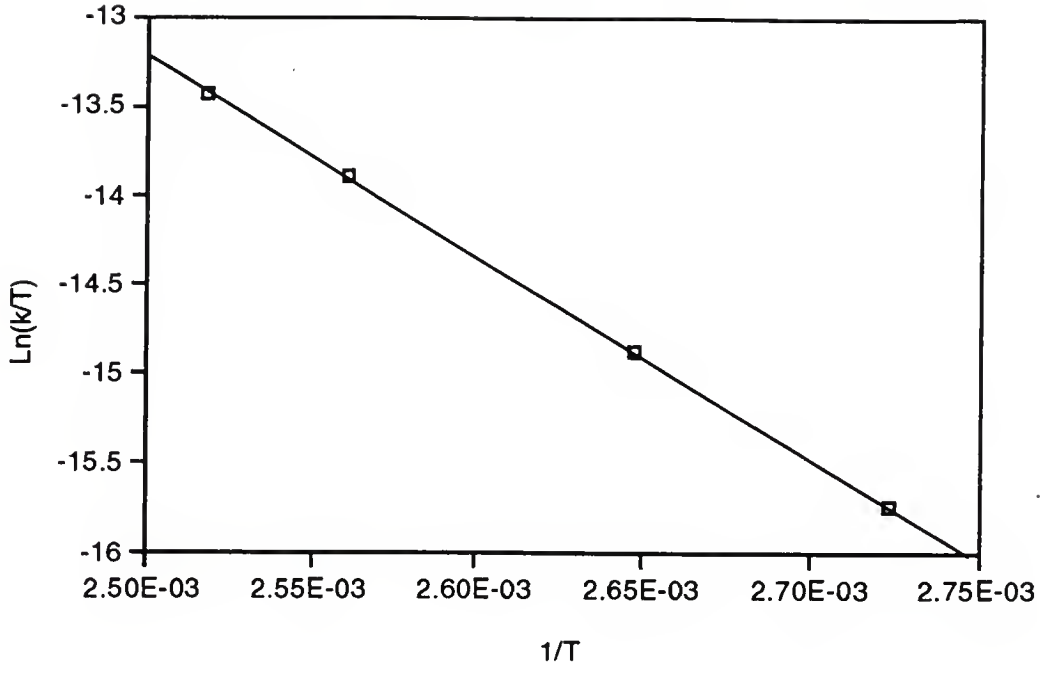


Figure 3-19. Eyring Plot for Thermolysis of *d,l*-1-(2-Difluoromethylidenecyclopentyl)-2-difluoromethylidenecyclopentane (***d,l*-131**).

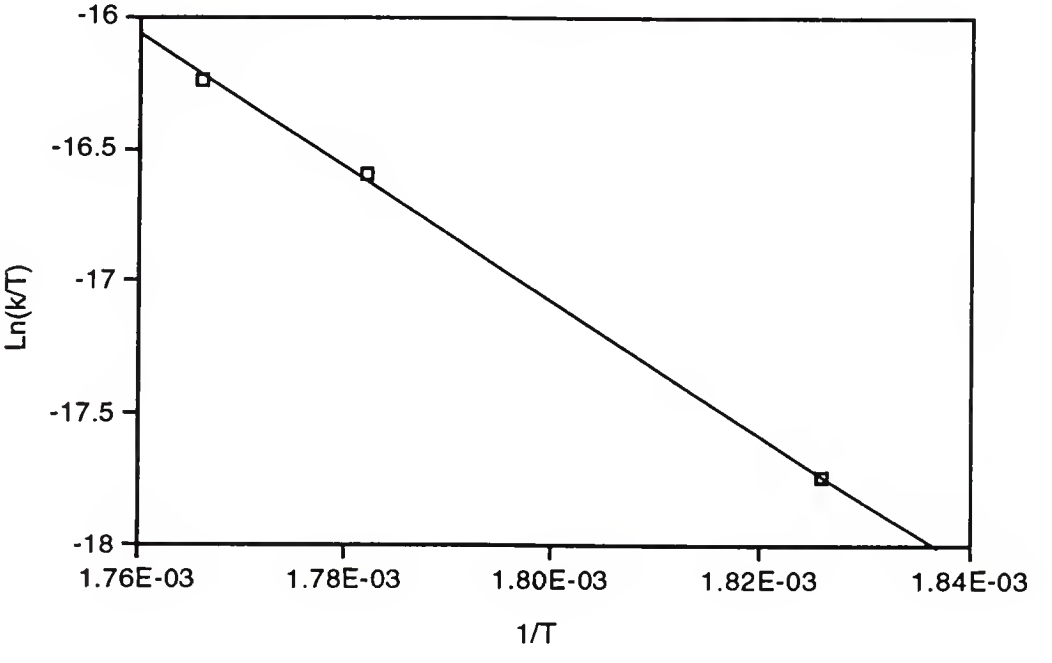
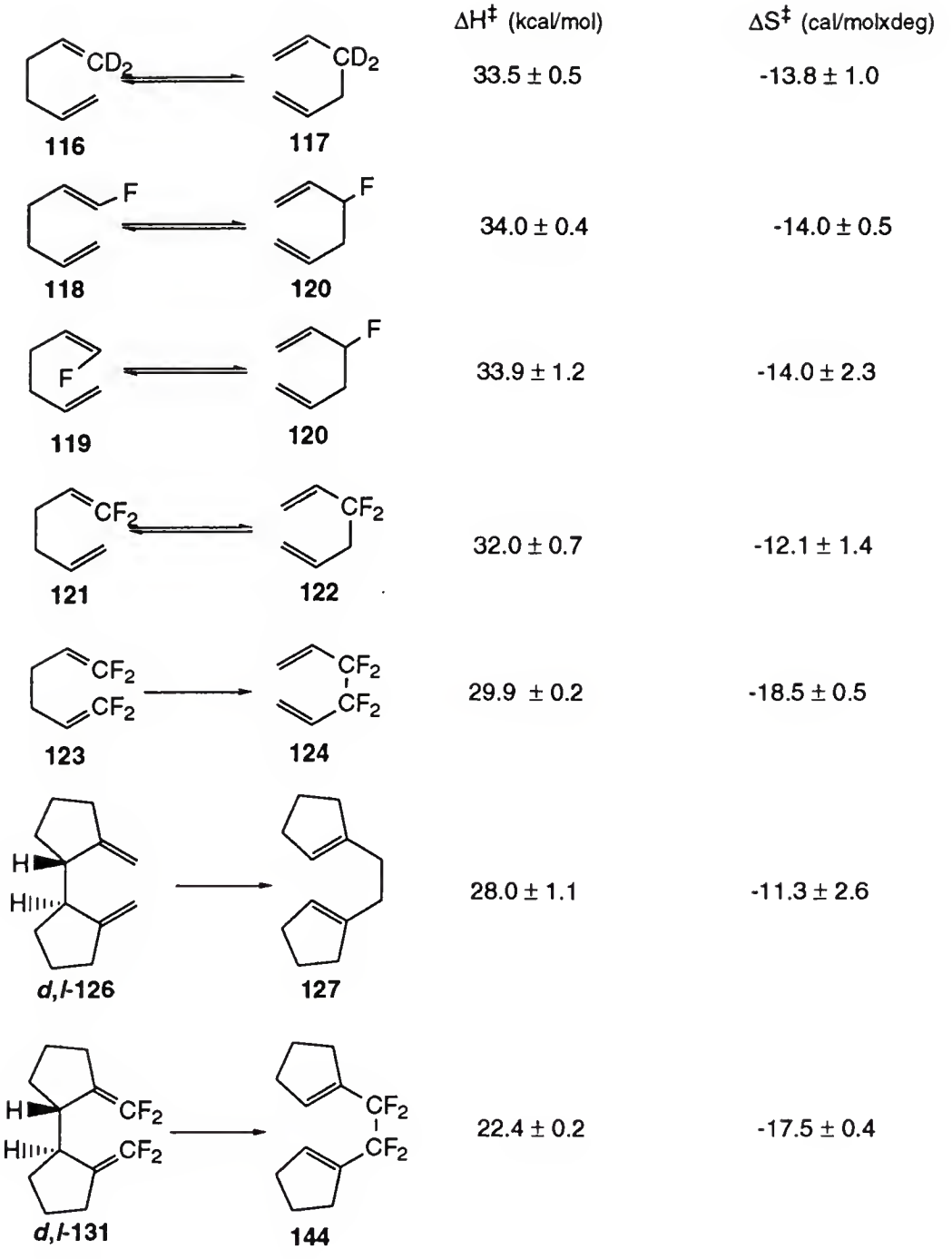


Figure 3-20. Eyring Plot for Thermolysis of *meso*-1-(2-Difluoromethylidenecyclopentyl)-2-difluoromethylidenecyclopentane (***meso*-131**).

mono-fluorination in the chair process. Within the error of the measurements, the activation enthalpy and entropy remain unchanged from the hydrocarbonvalues in the mono-fluorinated cases **118** and **119**. The *gem*-difluoro system **121** occurs with a 1.5 kcal/mol decrease in $\Delta H^{\ddagger}$ but no significant change in $\Delta S^{\ddagger}$ relative to the hydrocarbon. Two terminal *gem*-difluoro groups decrease $\Delta H^{\ddagger}$ by 3.6 kcal/mol from **116** to **123** and 5.6 kcal/mol from ***d,l*-126** to ***d,l*-131**. There is also a marked difference in the activation entropy for these two related processes; $\Delta S^{\ddagger}$ decreases by 4.7 cal/molxdeg from **116** to **123** and 6.2 cal/molxdeg from ***d,l*-126** to ***d,l*-131**.

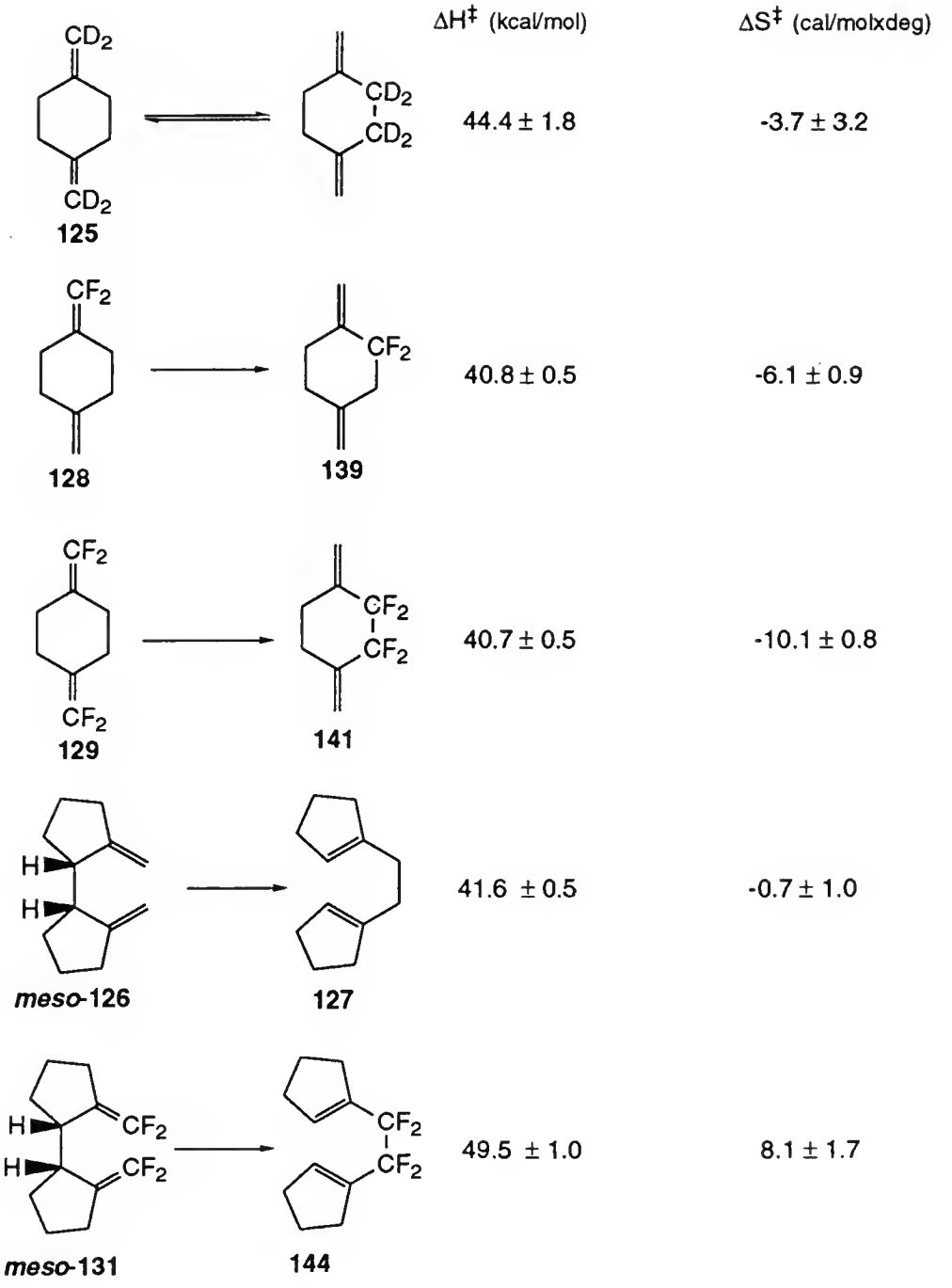
Figure 3-22 illustrates data for hydrocarbon and terminally fluorinated 1,5-diene systems from this study and literature constrained to boat transition state Cope rearrangements. The 1,4-dimethylenecyclohexane system exhibits an initial 3.6 kcal/mol decrease in $\Delta H^{\ddagger}$ and 2.4 cal/molxdeg decrease in $\Delta S^{\ddagger}$ upon introduction of one terminal *gem*-difluoromethylene group (**128** versus **125**). *Gem*-difluorination at both termini (**129**) shows no change in $\Delta H^{\ddagger}$ from the half fluorinated system (**128**), but $\Delta S^{\ddagger}$ decreases by 4.0 cal/molxdeg. The fluorinated meso-bismethylenecyclohexane system ***meso*-131**, exhibits increases in $\Delta H^{\ddagger}$ of 7.8 kcal/mol and $\Delta S^{\ddagger}$ of 8.8 kcal/molxdeg *versus* the hydrocarbon ***meso*-126**.

While discussing the kinetic effects of fluorination on these systems, it is important to keep in mind the fashion in which terminal fluorination will influence the thermodynamics of these Cope processes. The degeneracy of the process in 1,5-hexadiene and 1,4-dimethylenecyclohexane leads to no net enthalpy change upon rearrangement, although the deuterated materials (**116**, **125**) used to remove the degeneracy did exhibit $K_{eq(321.3°C)} = 2.19$ and $K_{eq} \approx 1.1$ respectively, due to secondary isotope effects. The hydrocarbon bis-methylenecyclopentane (**126**) was not observed to be reversible to any extent



References: **116**,[128] (**118**, **119**, **121**),[129] ***d,l*-126**,[132] **123** and ***d,l*-131**: This study.

Figure 3-21. Activation Parameters for Chair Transition State Cope Processes.



References: **125**,[131] **meso-126**,[132] All others (**128**, **129**, ***meso*-131**) from this study.

Figure 3-22. Activation Parameters for Boat Transition State Cope Processes.

indicating $\Delta H° > 5$ kcal/mol for **126**→**127** due to the formation of more substituted olefins. From the earlier discussion (Chapter 1) pertaining to fluorine's thermodynamic preference to be bonded to saturated carbon, it is expected that such a factor will impart anywhere from 2 to 5 kcal/mol exothermicity to the chair or boat type cyclizations for each *gem*-difluoroolefin. In fact, cyclization of **121**→**122** was observed to have $\Delta H° = -5$ kcal/mol.[129] As might be expected, the conversions of **123**→**124** and ***d,l*-131**→**144** are not reversible to any extent in line with simple additivity of the above indicated exothermicities for two such *gem*-difluoro groups. A similar situation is observed for the boat constrained systems in Figure 3-22.

With the precedent set for increasing exothermicity in each of these Cope series as the degree of terminal *gem*-difluorination is increased, it is not surprising that the series of fluorinated chair Cope processes examined show a steady decrease in $\Delta H^{\ddagger}$ as the number of terminal *gem*-difluoro groups increases. Such a trend is in line with the Hammond Postulate[138,139] in that an increasingly exothermic process will lead to an earlier transition state, one being more reactant-like in structure and energy. Any steric effect that fluorine imparts on the chair transition state (Figure 3-2) must then be minimal or non-existent, as increased fluorination showed only incremental decreases in $\Delta H^{\ddagger}$.

The trend of decreasing activation enthalpies based on changing relative thermodynamics with increasing degree of terminal *gem*-difluorination would be expected to be observed in the boat constrained Cope systems as it was in the chair systems if there was no detrimental steric influence due to fluorine. The series of terminally fluorinated 1,4-dimethylenecyclohexanes (**125**, **128**, **129**, Figure 3-22) seems to be showing a balance between thermodynamic based $\Delta H^{\ddagger}$ lowering and a kinetic destabilization of the transition state as the degree of terminal olefin *gem*-difluorination increases. The activation enthalpy decreases

from **125** to **128** and does not change from **128** to **129**, implying that the transition state involving coplanar eclipsed approach of the terminal carbons (Figure 3-4) is encountering some resistance. Physical overlap of the fluorines is unlikely in this case and resistance would most likely arise from difluoroolefin dipole or field repulsions. It is more likely though, that the decrease in activation entropy from **128** to **129** may explain the fact that $\Delta H^{\ddagger}$ is constant between these two systems. The decrease in activation entropy is consistent with a higher degree of bond formation between the terminal 1,5-diene carbons with minimal C2-C3 σ bond cleavage at the transition state of **129**. In effect, this is a higher degree of bicyclo[2.2.2]octane-1,4-diyl character which would impart more strain to the transition state in the tetrafluorinated (**129**) versus the difluorinated (**128**) case. If this increase in strain was influencing the transition state energy in a similar magnitude as the stabilizing effect of saturation of the additional difluoromethylene group, then as observed, one would expect no net change in the value of $\Delta H^{\ddagger}$ to occur between **128** and **129**.

In *meso*-1-(2-difluoromethylidenecyclopentyl)-2-difluoromethylidene-cyclopentane (***meso*-131**), the true boat conformation (Figure 3-2) allows for significant twisting in of two terminal *cis* substituents. The 7.8 kcal/mol increase in $\Delta H^{\ddagger}$ between ***meso*-126** and ***meso*-131** is believed to be due to strong repulsion between the two terminal *cis* fluorines directed at one another. It is also possible that this increase may be explained by a coplanar approach of the terminal olefinic carbons creating repulsion between hydrogens *endo* on the two cyclopentyl rings. It is difficult to postulate which situation will occur in the transition state of ***meso*-131**. Either way, the large increase in $\Delta H^{\ddagger}$ between ***meso*-126** and ***meso*-131** indicates that terminal *cis*-fluorination creates significant resistance to approach of terminal olefinic carbons through a boat conformation transition state. The activation enthalpy and entropy for this

rearrangement are the highest of the boat Cope systems observed. These energy parameters are consistent with a near-dissociative mechanism involving cleavage of the 1,5-diene C3-C4 bond (bond *a* in ***meso*-131**, Figure 3-23) to form a pair of allyl radicals (**145**) which may recombine to form the observed product **144** or potential [1,3]-shift adduct **146**. The dissociation energy ($\Delta H°_D$) for bond *a* in this system may be estimated by subtracting $\Delta H°_F$ = +6.4 kcal/mol for 3,4-dimethyl-1,5-hexadiene from twice the heat of formation of 1-butene-3-yl (2 x ($\Delta H°_F$ = +30.2 kcal/mol)).[59] This yields $\Delta H°_D \approx$ 54.0 kcal/mol for cleavage of this system to a pair of allylic radicals (**145**). Such an approximation is valid as each five membered ring is bonded to a nodal carbon in the allylic system and *gem*-difluorination has little effect on the stability of an allylic radical (Figure 1-5).[27]

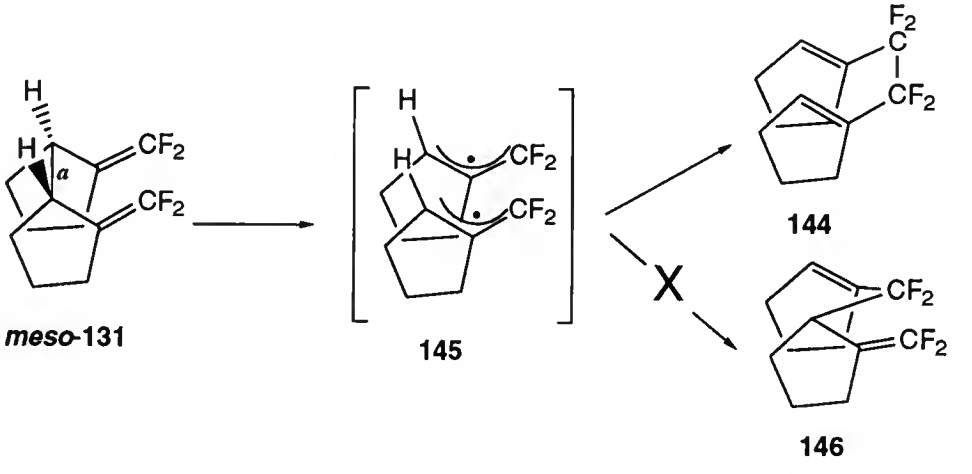


Figure 3-23. Thermal Rearrangement of *meso*-1-(2-Difluoromethylidene-cyclopentyl)-2-difluoromethylidenecyclopentane (***meso*-131**).

This excercise indicates that the observed process is occurring with an activation enthalpy 4.6 kcal/mol below that necessary for cleavage of ***meso*-131** to the hypothetical pair of allyl radicals (**145**). This difference can be thought of as the energy of concert for this boat conformation Cope process.

The activation entropies for both the chair and boat Cope processes are observed to become increasingly negative as the number of *gem*-difluoro groups increases (Figures 3-21 and 3-22) except as discussed in the case of ***meso*-131**. The 1,5-hexadiene systems, from hydrocarbon to terminally gem-difluorinated cases (**116**,**118**, **119**, and **121**), show similar $\Delta S^{\ddagger}$ values within the measured errors. Between 1,1-difluoro-1,5-hexadiene and 1,1,6,6-tetrafluoro-1,5-hexadiene (**121** and **123**) though, a 6.4 cal/molxdeg decrease is observed. A decrease is also observed between bismethylenecyclopentane systems ***d*,*l*-126** and ***d*,*l*-131** and down the series of dimethylenecyclohexanes, **125**, **128**, **129**; in all cases as the degree of terminal *gem*-difluorination is increased.

Such a substituent effect on the activation entropy of the Cope process has been previously observed in phenyl substituted diene systems and leads to the question of concert in the Cope process, which is a topic of current debate. One may envision the process as potentially occurring somewhere along a continuum involving concerted or one of two nonconcerted pathways. The nonconcerted extremes involve either the generation of two allyl radical fragments or formation of a 1,4-cyclohexanediyl. Two allyl radical fragments are argued to be too high in energy to possibly be involved in the Cope process of 1,5-hexadiene, as such a path occurring by C3-C4 bond homolysis requires an additional 24 kcal/mol in enthalpy above the transition state for the concerted process.[118] As a consequence, 1,3-shift products are not observed upon thermolysis of 1,5-dienes.

The 1,4-cyclohexanediyl alternative is the point of contention. Based on arguments that the heat of formation of bicyclo[2.2.0]hexane is 9 kcal/mol greater than 1,5-hexadiene and cleavage to 1,5-hexadiene occurs with $\Delta H^{\ddagger}$ = 36 kcal/mol, the cyclohexanediyl transition state is estimated to be 12 kcal/mol

higher in energy than the concerted structure and inaccessible to simple alkyl substituted 1,5-hexadienes.[54] This fact has been countered extensively by Dewar,[140,141] who through theoretical *ab initio* level study has argued the mechanism of the boat and chair processes are different. Dewar makes claim that the boat processes would be formally concerted and the concerted chair processes are actually occurring through a 1,4-cyclohexanediyl which involves strong "through bond coupling", making the transition state behave like a closed shell species. In contrast, there are those who argue in favor of the historical concerted process, such as Houk, who studied the system at the *ab initio* level and concluded concerted bond reorganization is occurring in the transition state.[118] Although disagreement is observed even with high levels of theory, these authors are consistent in agreeing that the mechanism of the Cope process will vary strongly across the possible allyl diradical/concerted/1,4-cyclohexanediyl spectrum depending on the electronic nature of substituents and their position of placement upon the 1,5-diene system.

The extent of bond making and bond breaking in the Cope rearrangement has been probed by observing secondary deuterium isotope effects in substituted 1,5-dienes.[54,142] From these results, it is generally agreed that radical stabilizing substituents at C2 and C5 lead to increased bond order between C1 and C6, in line with a 1,4-cyclohexanediyl type structure, and such substituents at C3 and C4 lead to transition states which more resemble a pair of allyl radicals. The notion of the 1,4-cyclohexanediyl has been further probed by comparison of the thermal chemistry of 2,6-diphenyl-1,6-heptadiene (**147**) and 2,5-diphenyl-1,5-hexadiene-*1,6*-$^{13}C_2$ (**150**)[143] Heptadiene **147** was termed a "frustrated" Cope system as it contains an additional methylene unit, making a concerted process impossible and offering a chance to probe the diradical. For **150**, it was found that $\Delta H^{\ddagger} = 22.0 \pm 0.18$ kcal/mol and

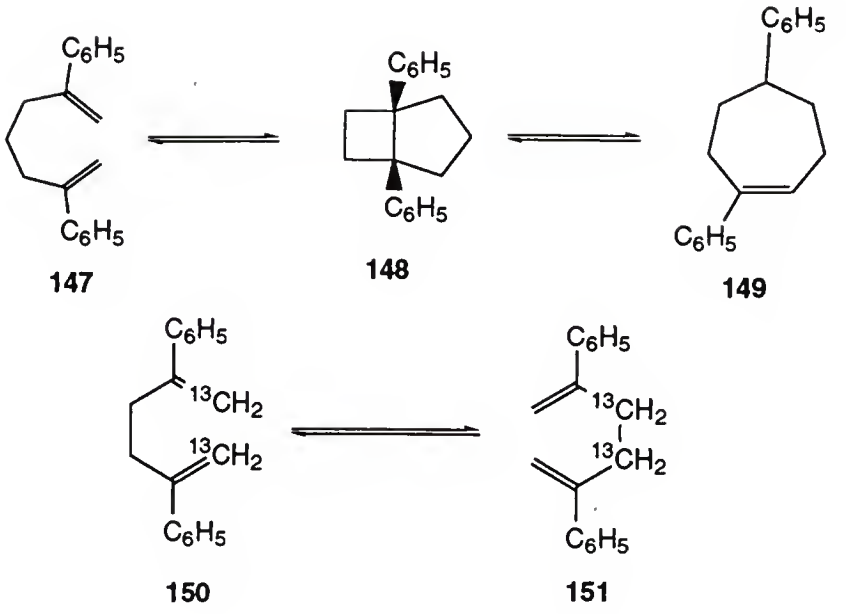


Figure 3-24. Thermal Rearrangements of 2,6-Diphenyl-1,6-heptadiene (**147**) and 2,5-Diphenyl-1,5-hexadiene-*1,6*-$^{13}C_2$ (**150**).

$\Delta S^{\ddagger}$ = -20.7 ± 0.4 cal/molxdeg and for **147** it was found that $\Delta H^{\ddagger}$ = 28.9 ± 0.6 kcal/mol and $\Delta S^{\ddagger}$ = -23.6 ± 1.1 cal/molxdeg. From this data and improved MM2 force field calculations, it was concluded that by introduction of benzyllic resonance into the 1,4-cyclohexanediyl, the diradical process occurs with an enthalpy of activation 14 kcal/mol below the concerted transition state for 1,5-hexadiene.

Recently the [3,3]-sigmatropic rearrangement of perfluoroallylvinyl ether to perfluoro-4-pentenal has been reported[144] with activation parameters $\Delta H^{\ddagger}$ = 18.5 kcal/mol and $\Delta S^{\ddagger}$ = -33.0 cal/molxdeg which differ significantly from the analogous hydrocarbon allylvinyl ether activation parameters[54] of $\Delta H^{\ddagger}$ = 25.7 kcal/mol and $\Delta S^{\ddagger}$ = -14.1 cal/molxdeg. A qualitative study (Figure 3-25) of perfluoro-1,5-hexadiene (**153**) and perfluoro-3-chloro-1,5-hexadiene (**155**) has also been recently reported.[145] At 250°C, **153** equilibrates with **152** with $K_{eq} \approx 0.7$, and at temperatures greater than 300°C, **154** is formed quantitatively

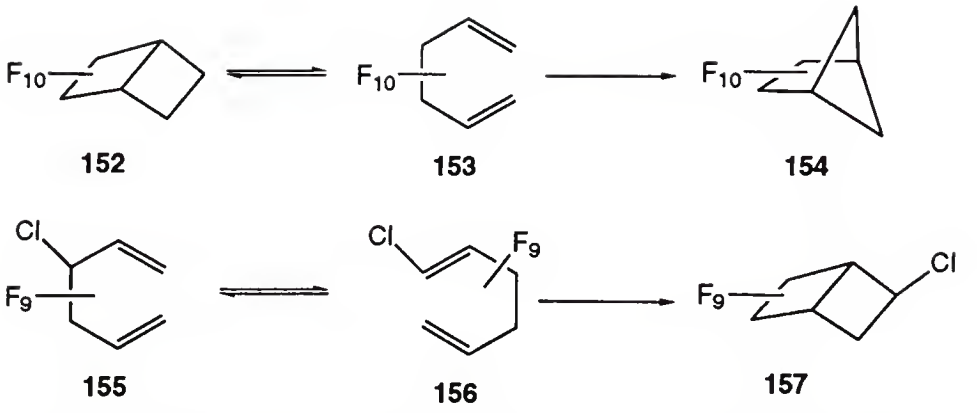


Figure 3-25. Thermal Rearrangements of Highly Fluorinated 1,5-Hexadienes.

from the mixture. Thermolysis of **156** leads to a mixture of **155** and **157** with the latter being the major reaction component. Since the formation of **152** and **157** require formation of a boat 1,4-cyclohexanediyl, it was tentatively concluded that the perfluorinated Cope system prefers initial boat conformation closure to such a diyl rather than closure through a chair followed by chair to boat conversion of the diyl, which was proposed to be impeded by "a large barrier". Formation of such a diyl may then be followed by bond formation to bicyclo[2.2.0]hexanes or ring opening to 1,5-cyclohexadienes. Such a process would seem unlikely in light of the strong disfavoring of such a transition state conformation observed with ***meso*-131**.

The increasingly negative activation entropies in the fluorinated Cope series (Figure 3-21 and 3-22) has limited precedent in the perfluoro Claisen rearrangement of perfluoroallylvinyl ether and is similar in trend to the C2 and C5 substituted hydrocarbon Cope systems which are argued to proceed through 1,4-cyclohexanediyl type intermediates. A mechanism involving a pair of allylic radicals is not consistent with the observed activation parameters as activation entropies and enthalpies would be expected to be larger than those

of corresponding hydrocarbons upon increasing fluorination and the stability of an allyl radical is known to be insensitive to partial fluorination (Figure 1-5).

It is more likely the case that the entropy of activation together with the enthalpy of activation data collected for the terminally *gem*-difluorinated 1,5-dienes, with the exception of ***meso*-131**, are indicating a concerted process which involves non-synchronous bonding changes at C1-C6 and C3-C4. The formation of the stronger and shorter σ bond in the case of the terminally tetrafluorinated 1,5-diene systems, would create a tighter transition state involving a higher degree of bond formation between C1-C6 than bond cleavage between C3-C4. Such non-synchronous bonding changes would impart radical character at the C2 and C5 positions. The changes in the activation parameters in these systems from those in the hydrocarbons must then be a result of the changing relative thermodynamics in these fluorinated systems as β-fluorination is known to stabilize radicals to a negligible degree[5] and therefore should not directly influence the transition state energy.

Conclusions

The influence of terminal *gem*-difluorination in pericyclic processes involving chair *versus* boat transition states is seen from these results to be fundamentally different. The chair type transition states are seen to accommodate terminal fluorine to any degree without detrimental kinetic effects. The changes in the activation parameters in this case can be attributed to changes in the relative thermodynamics of the 1,5-diene systems as the degree of terminal *gem*-difluorination is increased and are consistent with a mechanism involving a high degree of 1,5-diene C1-C6 bond formation with little C3-C4 bond cleavage. The boat type transition state is undergoing the same relative changes in thermodynamics upon increased fluorination, but the twisting in of

terminal *cis* fluorines in this conformation leads to highly repulsive interactions which give rise to activation parameters consistent with a transition state more resembling a pair of allyl radicals, involving a high degree of C3-C4 bond cleavage without a similar degree of C1-C6 bond formation.

CHAPTER 4

EXPERIMENTAL

General Methods

Nuclear magnetic resonance (NMR) chemical shifts are reported in parts per million (ppm) downfield (δ) from internal reference TMS for ^{1}H and ^{13}C spectra, and in ppm upfield (φ) from internal standard $CFCl_3$ for ^{19}F spectra. All NMR spectra were obtained on Varian VXR-300 or Varian XL-200 instruments. The format (field strength, solvent, reference) is included for all NMR spectra reported.

Gas chromatographic separations were performed by Gas-Liquid Phase Chromatography (GLPC) on packed columns. Quantitative GLPC was performed on a Hewlett Packard 5890 Series II gas chromatograph with a flame ionization detector and a Hewlett Packard 3396A integrator. Preparative GLPC was performed on a Varian Aerograph A-90 gas chromatograph equipped with a thermal conductivity detector. Conditions and columns used are discussed in relevant experimental sections.

Mass spectra and exact masses were determined on a Kraytos/AEI-30 spectrometer at 70 ev.

Ultra-violet (UV) spectra were obtained on an Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer.

Melting points were obtained on a Thomas Hoover Uni-Melt capillary melting point apparatus and are uncorrected.

Experimental text discussing a "dry" solvent indicates such material was purified (distilled) off of the appropriate drying agent and stored under an inert atmosphere. The following solvents and drying agents were used: dimethylformamide (CaH_2 or P_2O_5, ≈60°C/20 mm Hg), triglyme (CaH_2 or sodium benzophenone ketyl, 0.5 mm Hg), tetrahydrofuran (sodium benzophenone ketyl), diethyl ether (sodium benzophenone ketyl), n-alkanes (CaH_2). All other special preparations are discussed in the appropriate experimental section.

Experimental Procedures

Preparation of 9-Bromo-10-nitrophenanthrene (47)

9-Bromo-10-nitrophenanthrene (**47**) was prepared by adaptation of a procedure as described by Callow and Gulland.[64] 9-Bromophenanthrene[63] (26.33 g, 1.025×10^{-1} mol) was dissolved in 60 ml of glacial acetic acid in a 250 ml, three neck, round bottom flask equipped with a magnetic stirrer, stopper, and a condenser with a piece of polyethylene tubing for directing nitrogen oxides evolved up into the hood. 30 ml of acetic anhydride was added, and the mixture was warmed to 90°C. Concentrated (70%, 10 ml) nitric acid was placed in the addition funnel and added dropwise with vigorous stirring over 30 minutes. Upon completion of addition, the mixture was heated at a gentle reflux for 1 hour. Analysis of the mixture by TLC (Merck Kieselgel 60 F_{254} glass backed plates) in 2.5 hexanes/1 CH_2Cl_2 showed eight spots. R_f values: 0.64 (w, 9-bromophenanthrene), 0.39 (w), 0.36 (s), 0.29 (w), 0.25 (m), 0.20 (m), 0.11 (w), 0 (w). After the reflux period, the reaction mixture was allowed to cool to room temperature and an amorphous, deep brick-red solid fell out of a solution of the same color. This material was recrystallized from acetone, CCl_4, then twice from methyl ethyl ketone. Crystalline **47** is afforded pure from the last recrystallization in methyl ethyl ketone as 8.01 g (25.9%) light yellow needles

melting 202-204°C (Lit. 195°C),[64] with R_f = 0.36 in the above solvent system. A fine yellow precipitate was obtained out of the CCl_4 and first methyl ethyl ketone filtrates, R_f = 0.36 (weak) and 0.25 (strong). One further recrystallization from methyl ethyl ketone yields 3.0 g (13.2%) pale yellow crystals of 9-bromo-3-nitrophenanthrene melting 189-190°C, with R_f = 0.25 in the above solvent system.

9-Bromo-10-nitrophenanthrene (**47**): ^{1}H NMR (300 MHz, $CDCl_3$, TMS) 7.60-7.82 (m, 5H), 8.41 (d with fine splitting, 1H, $^3J_{HH}$ = 8.0 Hz, J_{HH} = 1.74 Hz), 8.65 (d, 1H, $^3J_{HH}$ = 7.80 Hz), 8.66 (d, 1H, $^3J_{HH}$ = 8.02 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) 113.1, 122.2, 122.9, 123.1, 123.5, 128.5, 128.7, 128.7, 129.3, 129.3, 130.1, 130.6; Low Resolution Mass Spectrum: m/z (% relative intensity) 303 (27), 301 (28), 245 (28), 243 (29), 222 (16), 178 (18), 177 (18), 176 (100), 164 (21), 163 (18), 150 (18)

9-Bromo-3-nitrophenanthrene: ^{1}H NMR (300 MHz, $CDCl_3$, TMS) 7.81 (m, 2H), 7.90 (d, 1H, $^3J_{HH}$ = 8.78 Hz), 8.16 (s, 1H), 8.38 (d, 1H, $^3J_{HH}$ = 8.7 Hz), 8.43 (d, 1H, $^3J_{HH}$ = 8.56 Hz), 8.73 (d, 1H, $^3J_{HH}$ = 9.4 Hz), 9.53 (d, 1H, $^4J_{HH}$ = 2.18 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) 119.3, 121.2, 123.2, 126.7, 128.7, 128.8, 128.9, 129.0, 129.5, 130.9, 131.2, 135.6; Low Resolution Mass Spectrum: m/z (% relative intensity) 303 (52), 302 (8), 301 (49), 245 (12), 243 (12), 177 (16), 176 (100), 175 (16), 174 (13), 150 (13), 88 (14), 87 (9)

Preparation of 9-Iodo-10-nitrophenanthrene (**48**)

9-Bromo-10-nitrophenanthrene (**47**, 1.0 g, 3.3×10^{-3} mol), dry NaI (5.64 g, 3.76×10^{-2} mol), and 40 ml of DMF were combined in a 100 ml, three neck, round bottom flask equipped with a magnetic stirrer, condenser, and two stopcocks. The reaction mixture was brought to a gentle reflux for 16 hours while following the reaction by TLC (Merck Kieselgel 60 F_{254} glass backed plates) in 2.5

hexanes/1 CH_2Cl_2. After 16 hours, TLC shows one major and two minor products. R_f = 0.32 (s), 0.1 (w), 0 (m). (9-bromo-10-nitrophenanthrene has R_f = 0.36 in the same system.) The reaction mixture was cooled and added to a separatory funnel containing 250 ml of water. The aqueous mixture was extracted with diethyl ether (4 x 150 ml). The ether extracts were combined and washed with 3 x 250 ml of water. The ether solution was dried over anhydrous $MgSO_4$, and distilled by rotary evaporator to yield 0.49 g (42%) burnt-orange crystals of **48** melting 196-198°C (Lit.198-200°C).[65]

9-Iodo-10-nitrophenanthrene (**48**): ^1H NMR (300 MHz, $CDCl_3$, TMS) 7.58-7.78 (m, 5H), 8.31 (d with fine splitting, 1H, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.5 Hz), 8.59 (d, 1H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz), 8.66 (d, 1H, $^3J_{HH}$ = 7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) 122.3, 122.5, 122.9, 123.1, 123.7, 128.6, 128.7, 128.9, 129.1, 129.3, 130.0, 130.7, 130.8, 134.9; Low Resolution Mass Spectrum: m/z (% relative intensity) 350 (12), 349 (75), 291 (16), 192 (12), 178 (11), 177 (17), 176 (100), 164 (30), 163 (15), 150 (16), 88 (14); Elemental Analysis on $C_{14}H_8INO_2$ Calculated %: C:48.17, H:2.31, N:4.01, Measured %: C:48.47, H:2.21, N:3.86

Preparation of Iodotrifluoroethylene

Iodotrifluoroethylene was either purchased from Peninsular Chemicals Research, Gainesville, Florida, or prepared by the method of Hansen.[70] Flame dried apparatus was assembled under N_2 purge as follows: 1 liter, three neck, round bottom flask fitted with cold finger condenser, jacketed addition funnel, stopper, and magnetic stirrer. Acid activated zinc powder (32.8 g, 0.502 mol) was added to the reaction vessel followed by 500 ml of dry DMF. $BrFC=CF_2$ (90.0 g, 0.559 mol) was condensed into the dry-ice/isopropyl alcohol cooled, jacketed addition funnel from a tared Rotaflow tube. The $BrFC=CF_2$ was added

drop-wise over 30 minutes and the reaction vessel was cooled with an ice-water bath to contain the generated exotherm. Upon completion of addition, the mixture was stirred for 1 hour, then the condenser was replaced with a vacuum takeoff. A liquid N_2 cooled, two necked Rotaflow trap was placed between the vacuum pump and reaction vessel and the reaction mixture was evacuated for 30 minutes at 0.1 mm Hg to remove and trap unreacted $BrFC=CF_2$. The reaction vessel was then refitted with the condenser and N_2 purge and 127.0 g (1.0 mol) of I_2 was added from a solid addition tube to the reaction vessel over 10 minutes while cooling the mixture with an ice-water bath. After the I_2 addition was complete, the cooling bath was removed and the mixture was stirred rapidly for 3 hours at room temperature. The condenser was then replaced with a vacuum takeoff and a two necked Rotaflow trap cooled with liquid N_2 was placed between the vacuum pump and the reaction vessel. The reaction mixture was then flash distilled at room temperature. The $IFC=CF_2$ distillate was rinsed with 2 x 200 ml of ice-water, keeping the trap in ice at all times. Water floated over the $IFC=CF_2$ and was removed by cannula using a positive pressure of N_2 over the liquid. The $IFC=CF_2$ was then vacuum transferred into an evacuated Rotaflow tube containing 4 Å sieves. Low boiling (reported boiling point of 30-32°C) clear liquid (58.7 g, 56%) , gradually turning pink, was obtained. ^{19}F NMR of this material is consistent with samples obtained from Peninsular Chemicals Research, Gainesville, Florida.

Iodotrifluoroethylene: ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$) -84.4 (dd, 1F, $^2J_{FF}$ = 64.3 Hz, $^3J_{cisFF}$ = 51.3 Hz), -109.9 (dd, 1F, $^3J_{transFF}$ = 128.9 Hz, $^2J_{FF}$ = 64.3 Hz), -146.7 (dd, 1F, $^3J_{transFF}$ = 128.9 Hz, $^2J_{FF}$ = 51.3 Hz)

Preparation of $ZnIFC=CF_2$ and $Zn(CF=CF_2)_2$

$ZnIFC=CF_2$ and $Zn(CF=CF_2)_2$ solutions were prepared by the method of Heinze and Burton.[66] An 100 ml, 2 neck, round bottom flask with a magnetic stirrer, stopper, and septum was flame dried under Ar purge. Acid activated Zn powder (8.6 g, 0.13 mol) was added followed by 300 ml of dry triglyme. The mixture was stirred rapidly and cooled to 0°C. $IFC=CF_2$ (5.61 g, $2.70x10^{-2}$ mol) was added by cannula from a tared bottle. After 12 hours stirring at room temperature, the solution had turned a maple syrup brown from initially clear and colorless. The yield (based on starting $IFC=CF_2$ by ^{19}F NMR *versus* internal standard) is 82% and the ratio of *mono* to *bis*-trifluoroethenylsubstituted Zn reagent is 3:2.

$ZnIFC=CF_2$ and $Zn(CF=CF_2)_2$: ^{19}F NMR (282 MHz, triglyme, $CFCl_3$) *mono*: -94.7 (dd, 1F, $^2J_{FF}$ = 91 Hz, $^3J_{cisFF}$ = 33 Hz), -128.4 (dd, 1F, $^3J_{transFF}$ = 106 Hz, $^2J_{FF}$ = 91 Hz), -193.3 (dd, 1F, $^3J_{transFF}$ = 106 Hz, $^2J_{FF}$ = 33 Hz), *bis*: -95.4 (dd, 1F, $^3J_{cisFF}$ = 33 Hz, $^2J_{FF}$ = 92 Hz), -129.4 (dd, 1F, $^3J_{transFF}$ = 105 Hz, $^2J_{FF}$ = 92 Hz), -194.6 (dd, 1F, $^3J_{transFF}$ = 105 Hz, $^2J_{FF}$ = 33 Hz)

Preparation of 9,10-Bis(trifluoroethenyl)phenanthrene (**40**)

9,10-bis(trifluoroethenyl)phenanthrene (**40**) was prepared by adaptation of a procedure as described by Heinze and Burton.[66] Apparatus as follows was flame dried under N_2 purge: 100 ml, three neck, round bottom flask fitted with a septum, glass stopper, condenser with N_2 purge, and a magnetic stirrer. Dry triglyme (15 ml) was added by syringe followed by 0.400 g ($1.14x10^{-3}$ mol) 9-iodo-10-nitrophenanthrene (**48**), 0.070 g ($5.7x10^{-5}$ mol) $Pd(P(C_6H_5)_3)_4$ (weighed in drybox and transferred by solid addition tube) and 6.0 ml of perfluoroethenyl zinc iodide solution ($-CF=CF_2$ concentration is 0.65 M by internal standard ^{19}F NMR, 6.0 ml is $3.9x10^{-3}$ mol) by syringe. The mixture was

stirred and heated to 110-112°C. After 7.5 hours, 9-iodo-10-nitrophenanthrene is consumed as indicated by TLC (Merck Kieselgel 60 F_{254} glass backed plates) in 8 hexane/3 THF. Seven spots are evident: R_f = 0.57 (s), 0.44 (w), 0.42 (w), 0.32 (w), 0.26 (w), 0.23 (s), 0.14 (m). The reaction mixture was decanted from a small amount of black solid into a separatory funnel and diluted with 300 ml of water, then extracted with 5 x 100 ml of diethyl ether. The ether extracts were then combined and washed with 5 x 100 ml of water. The ether solution was dried over anhydrous $MgSO_4$ then concentrated by rotary evaporator to yield 0.20 g of brownish-yellow solid. This solid was dissolved in ether and 5 g of silica gel was added, then the ether evaporated under a stream of N_2. The dry reaction mixture deposited on silica gel was taken up in hexanes and added to a 2 x 30 cm silica gel column packed by slurry in hexanes. The column was eluted under flash conditions with hexanes, 9 hexanes/1 THF, and last acetone. 0.063 g (16.2%) **40** was obtained as white flakes melting 133-134°C, R_f = 0.57 in the above solvent system. Other fractions were not pure and accounted for 0.176 g material, which were not further analyzed.

Purification of 9,10-Bis(trifluoroethenyl)phenanthrene (**40**) by Preparative GLPC

The coupling reaction was carried out using similar conditions as described previously using 1.0 g 9-iodo-10-nitrophenanthrene (**48**). Extractions were carried out as in the previous preparation and the resultant 0.55 g brown oil was dissolved in 0.5 ml of diethyl ether and separated by preparative GLPC in 50 µl aliquots. (Column: 0.25 inch x 5 feet, 20% QF-1 on Chromasorb WHP 80/100; Oven: constant at 193°C; Injector: 245°C; TCD block: 232°C; He flow : 120 ml/minute; **40** retention time: 11.0 minutes) White flakes of

40 (0.143 g, 15%) were obtained melting at 134°C. The purity of this material is ≈100% by analytical GLPC.

9,10-Bis(trifluoroethenyl)phenanthrene (**40**): ^{1}H NMR (300 MHz, $CDCl_3$, TMS) 7.67 (t, 2H, $^{3}J_{HH}$ = 8.0 Hz), 7.75 (t, 2H, $^{3}J_{HH}$ = 8.0 Hz), 8.07 (d, 2H, $^{3}J_{HH}$ = 8.1 Hz), 8.68 (d, 2H, $^{3}J_{HH}$ = 8.1 Hz); ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$, 22°C) *syn* diasteromer: low field (≈ -100) signal overlapped with *anti* diastereomer, -115.7 (dd, 2F, $^{3}J_{transFF}$ = 117 Hz, $^{2}J_{FF}$ = 75 Hz), -159.3 (dd, 2F, $^{2}J_{FF}$ = 75 Hz, $^{3}J_{cisFF}$ = 20 Hz), *anti* diasteromer: -100.2 (dd, 2F, $^{2}J_{FF}$ = 70.9 Hz, $^{3}J_{cisFF}$ = 27.1 Hz), -115.0 (dd, 2F, $^{3}J_{transFF}$ = 119.1 Hz, $^{2}J_{FF}$ = 70.9Hz), -160.6 (dd, 2F, $^{2}J_{FF}$ = 70.9 Hz, $^{3}J_{cisFF}$ = 27.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) 123.0, 126.6 (bm), 127.9, 129.1, 131.6; UV Spectrum in *n*-pentane: $\lambda_{(nm)}$ ($E_{(cm^2/mol)}$), 209 (23742.6), 224 (25146.7), 257 (49706.5), 295 (10428.9), 306 (11760.7); Low Resolution Mass Spectrum: m/z (% relative intensity) 339 (17), 338 (100), 288 (80), 287 (19), 269 (89), 267 (17), 238 (15), 134 (17); High Resolution Mass Spectrum: Calculated for $C_{18}H_8F_6$ = 338.0530, Measured = 338.0539

Thermolysis of 9,10-Bis(trifluoroethenyl)phenanthrene (**40**): Isolation of Products 1,2,2,3,3,4-Hexafluoro-2,3-dihydrotriphenylene (**41**), 1,4,4,5,6,6 Hexafluoro-2,3-(9,10-phenanthro)bicyclo[3.1.0]hex-2-ene (**49**), 4-Difluoro methylidene-3,3,5,5-tetrafluoro-1,2-(9,10-phenanthro)cyclopent-1-ene (**50**), and 1,2-(9,10-Phenanthro)-3,5,5-trifluoro-4-trifluoromethyl-1,3-cyclopentadiene (**51**)

A solution of 0.076 g ($2.2x10^{-4}$ mol) **40** in 1.9 g C_6H_6 was prepared and flame sealed in a Carius tube under N_2. The sample was then placed in a Statim thermostated oil bath at 180°C and heated for 54 hours. The tube was opened and GLPC analysis showed starting material and four new products (Column: 0.125 inch x 10 feet, 20% QF-1 on Chromasorb WHP 100/120; Oven: constant at 205°C; Injector: 210°C); percentages of total mass balance being: 20% **40**, 7% **49**, 6% **50**, 10% **41**, and 57% **51**. The solvent was evaporated under a stream of N_2, then the sample was subject to vacuum (0.1 mmHg for 1

hour) to yield 0.066 g of yellowish-tan powder, corresponding to an 86% yield of $C_{18}H_8F_6$ isomers. This mixture was taken up in 0.5 ml diethyl ether and separated into five fractions by preparative GLPC, for a 54% yield of $C_{18}H_8F_6$ isomers isolated. (Column: 0.25 inch x 5 feet, 20% QF-1 on Chromasorb WHP 80/100; Oven: constant at 193°C; Injector: 245°C; TCD block: 232°C; He flow : 120 ml/minute; Retention times: Compound (minutes), **40** (11.0), **49** (16.5), **50** (18.3), **41** (22.5), **51** (30.5))

Fraction 1: By comparison of ^1H and ^{19}F NMR spectra and melting point with earlier obtained sample, the material is found to be **40**. White flakes (6 mg, 9% isolated) were obtained melting 132-134°C and ≈100% pure by analytical GLPC.

Fraction 2: 1,4,4,5,6,6-Hexafluoro-2,3-(9,10-phenanthro)bicyclo[3.1.0]-hex-2-ene (**49**): White powder (2 mg, 3% isolated) was obtained, actually a 2:1 mixture of **49** and **50**. A second careful separation of such a mixture by the aforementioned preparative GLPC conditions would yield ratios around 24:1, respectively. 1,4,4,5,6,6-Hexafluoro-2,3-(9,10-phenanthro)-bicyclo[3.1.0]hex-2-ene (**49**): ^1H NMR (300MHz, $CDCl_3$, TMS) 7.72-7.86 (m, 4H), 8.25-8.30 (m, 2H), 8.74 (d, 1H, $^3J_{HH}$ = 8.4 Hz), 8.76 (d, 1H, $^3J_{HH}$ = 8.4 Hz); ^{19}F NMR (188 MHz, $CDCl_3$, $CFCl_3$) -87.8 (dddm, 1F, $^2J_{FF}$ = 267.3 Hz, $^3J_{FF}$ = 13.7 Hz, $^4J_{FF}$ = 3.4 Hz), -112.4 (dm, 1F, $^2J_{FF}$ = 268.0 Hz), 137.7 (dddm, 1F, $^2J_{FF}$ = 173.2 Hz, $^3J_{FF}$ = 13.7 Hz, $^4J_{FF}$ = 5.7 Hz), -147.7 (dtd, 1F, $^2J_{FF}$ = 173.2 Hz, $^3J_{FF}$ = 15.3 Hz, $^4J_{FF}$ = 7.6 Hz), -216.1 to -216.4 (m, 1F), -230.2 (ddddd, 1F, $^3J_{FF}$ = 28.3 Hz, $^3J_{FF}$ = 15.1 Hz, $^3J_{FF}$ = 8.2 Hz, $^4J_{FF}$ = 4.2 Hz, $^4J_{FF}$ = 1.0 Hz); Low Resolution Mass Spectrum: m/z (% relative intensity) 339 (16), 338 (97), 288 (71), 287 (16), 269 (97), 238 (17),134 (29), 119 (49); High Resolution Mass Spectrum: Calculated for $C_{18}H_8F_6$ = 338.0530, Measured = 338.0547

Fraction 3: 4-Difluoromethylidene-3,3,5,5-tetrafluoro-1,2-(9,10-phenanthro)cyclopent-1-ene (**50**): A light yellow powder (4 mg, 5% isolated) being a 32.3:1 mixture of **50** and **51** was obtained. 4-Difluoromethylidene-3,3,5,5-tetrafluoro-1,2-(9,10-phenanthro)cyclopent-1-ene (**50**): ^{1}H NMR (300 MHz, $CDCl_3$, TMS) 7.77 (t with fine splitting, 2H, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.4 Hz), 7.68 (t with fine splitting, 2H, $^3J_{HH}$ = 7.1 Hz, $^4J_{HH}$ = 1.4 Hz), 8.39 (d, 2H, $^3J_{HH}$ = 7.7 Hz), 8.78 (d with fine splitting, 2H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.4 Hz); ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$) -70.56 to -70.65 (m, 2F), -89.6 (ddm, 4F, $^4J_{FF}$ = 3.9 Hz, $^4J_{FF}$ = 3.3 Hz); Low Resolution Mass Spectrum: m/z (% relative intensity) 339 (18), 338 (100), 319 (36), 269 (39), 159 (18), 134 (22); High Resolution Mass Spectrum: Calculated for $C_{18}H_8F_6$ = 338.0530, Measured = 338.0552

Fraction 4: 1,2,2,3,3,4-Hexafluoro-2,3-dihydrotriphenylene (**41**): A light yellow solid (4 mg, 5% isolated) 85% pure with contamination by 3% **50** and 12% **51** was obtained. 1,2,2,3,3,4-Hexafluoro-2,3-dihydrotriphenylene (**41**): ^{1}H NMR (300MHz, $CDCl_3$, TMS) 7.38 (t, 2H, $^3J_{HH}$ = 8.7 Hz), 7.47 (t, 2H, $^3J_{HH}$ = 8.7 Hz), 7.93 (d, 2H, $^3J_{HH}$ = 8.4 Hz), 8.06 (d, 2H, $^3J_{HH}$ = 8.4 Hz); ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$) -132.6 (dm, 4F, $^3J_{FF}$ = 12.4 Hz), -135.9 (tm, 2F, $^3J_{FF}$ = 12.4 Hz); Low Resolution Mass Spectrum: m/z (% relative intensity) 339 (14), 338 (90), 288 (45), 287 (72), 238 (12), 134 (27), 124 (13), 119 (24); High Resolution Mass Spectrum: Calculated for $C_{18}H_8F_6$ = 338.0530, Measured = 338.0540

Fraction 5: 1,2-(9,10-Phenanthro)-3,5,5-trifluoro-4-trifluoromethyl-1,3-cyclopentadiene (**51**): Light yellow needles (24 mg, 32% isolated) were obtained. A second seperation of such material by the previous preparative GLPC conditions could yield material ≈100% pure by analytical GLPC, melting 125-126°C. 1,2-(9,10-Phenanthro)-3,5,5-trifluoro-4-trifluoromethyl-1,3-cyclopentadiene (**51**): ^{1}H NMR (300 MHz, $CDCl_3$, TMS) 7.76 (t, 2H, $^3J_{HH}$ = 8.4 Hz), 7.81 (t, 2H, $^3J_{HH}$ = 8.4 Hz), 8.30 (d, 1H, $^3J_{HH}$ = 8.0 Hz), 8.40 (d, 1H, $^3J_{HH}$ = 8.1

Hz), 8.76 (d, 1H, $^3J_{HH}$ = 8.3 Hz), 8.78 (d, 1H, $^3J_{HH}$ = 8.4 Hz); ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$) -59.3 (dt, 3F, $^4J_{FF}$ = 14.1 Hz, $^4J_{FF}$ = 2.3 Hz), -103.7 (m,1F), -121.6 (dm, 2F, $^4J_{FF}$ = 8.7 Hz); Low Resolution Mass Spectrum: m/z (% relative intensity) 339 (17), 338 (100), 319 (12), 270 (9), 269 (64), 249 (10); High Resolution Mass Spectrum: Calculated for $C_{18}H_8F_6$ = 338.0530, Found = 338.0518

Solution Phase Thermolysis of 9,10-Bis(trifluoroethenyl)phenanthrene (**40**): A Quantitative Study Followed by ^{19}F NMR

A stock solution of **40** in C_6D_6 was prepared as follows: 0.0481 g (1.42×10^{-4} mol) preparative GLPC purified **40** (GLPC conditions as in previous synthetic section) was dissolved in 1.1 ml of C_6D_6 and 7 mg C_6H_5F was added as an ^{19}F NMR internal standard. An aliquot of the solution was syringed into each of three thick walled NMR tubes (base rinsed, deionized water rinsed, acetone rinsed, flame dried) and then the tubes were flame sealed under N_2. Thermolysis was carried out by submerging the sample in a Statim thermostated oil bath for a time period then rapidly removing and cooling the sample in an ice bath. The sample was then observed by ^{19}F NMR using a T_1 delay of 10 seconds and collecting a minimum of 128 transients before Fourier transforming the spectrum. The relative concentrations of all fluorinated products was arrived at by integration of the sample signals and comparison *versus* the internal standard C_6H_5F. (See Tables 4-1, 4-2, and 4-3 for data.)

Solution Phase Thermolysis of 1,4,4,5,6,6-Hexafluoro-2,3-(9,10-phenanthro)-bicyclo[3.1.0]hex-2-ene (**49**): A Quantitative Study Followed by ^{19}F NMR

A stock solution of **49** in C_6D_6 was prepared as follows: 0.0078 g (2.3×10^{-5} mol) preparative GLPC purified **49** (preparative GLPC as in synthetic discussion section, containing traces of **50** and **51**) was dissolved in 0.52 g

Table 4-1. Relative Percent Composition Data for Thermolysis of **40** at 180.0°C.

Seconds	%40	%49	%50	%41	%51	%MB
0	100.0	0	0	0	0	-
5040.	94.20	4.87	0	0.91	0	-
18960.	80.15	13.57	1.68	2.52	1.08	-
33360.	73.26	16.48	3.35	5.08	1.84	-
37920.	67.73	18.08	4.67	5.81	3.69	-
66720.	51.05	20.45	11.17	9.28	8.04	100
82560.	44.62	20.45	14.36	10.53	10.03	98.4
105060.	35.33	19.68	19.80	11.61	13.56	97.6
112980	33.61	17.65	21.42	12.37	14.95	95.9
183060	15.83	11.48	34.28	14.68	23.71	94.6
264300	7.56	5.41	41.94	14.16	30.93	90.8
445980	0	0	42.14	12.05	45.81	83.7
598740	0	0	22.34	9.13	68.52	83.2
665700	0	0	12.19	7.66	80.15	81.1
716520	0	0	4.93	6.95	88.12	80.0
844500	0	0	0	4.59	95.41	77.8

Table 4-2. Relative Percent Composition Data for Thermolysis of **40** 184.5°C.

Seconds	%40	%49	%50	%41	%51	%MB
0	100.0	0	0	0	0	-
16920	76.22	14.99	1.49	3.98	3.34	-
26160	66.43	18.41	1.93	5.67	7.56	-

Table 4-2 - Continued-

Seconds	%40	%49	%50	%41	%51	%MB
38820	54.60	20.37	3.55	7.56	13.92	-
42840	51.32	20.35	3.72	8.07	16.54	-
59520	39.59	19.35	8.23	9.73	23.10	96.7

Table 4-3. Relative Percent Composition Data for Thermolysis of **40** 193.0°C.

Seconds	%40	%49	%50	%41	%51	%MB
0	100.0	0	0	0	0	
7200.	76.69	14.94	1.78	3.82	2.76	
15840.	58.97	19.99	2.53	6.84	11.67	
22620.	48.14	20.10	1.55	8.49	21.70	
33180.	35.35	17.72	1.16	10.48	35.29	
45000.	24.85	13.84	1.03	11.71	48.56	
60900.	16.67	9.34	0.87	12.07	61.04	100

C_6D_6 and 10 mg of C_6F_6 was added as an ^{19}F NMR internal standard. An aliquot of the solution was syringed into each of three thick walled NMR tubes (base rinsed, deionized water rinsed, acetone rinsed, flame dried) and then the tubes were flame sealed under N_2. Thermolysis was carried out by submerging a sample in a Statim thermostated oil bath for a time period then rapidly removing and cooling the sample in an ice bath. The sample was then observed by ^{19}F NMR using a T_1 delay of 10 seconds and collecting a minimum of 128 transients before Fourier transforming the spectrum. The relative concentrations of all fluorinated products was arrived at by integration of the

sample signals and comparison *versus* the internal standard C_6F_6. (See Tables 4-4, 4-5, and 4-6 for data.)

Table 4-4. Relative Percent Composition Data for Thermolysis of **49** at 180.0°C.

Seconds	%49	%50	%51	%MB
0	90.69	7.63	1.68	-
9660.	74.71	17.50	7.79	-
14220.	68.66	21.19	10.14	-
21000.	60.33	26.48	13.18	-
27780.	51.72	31.14	17.14	-
38220.	42.61	37.41	19.90	-
45420.	37.37	40.54	22.09	-
52800.	32.14	43.78	24.08	100

Table 4-5. Relative Percent Composition Data for Thermolysis of **49** at 185.0°C.

Seconds	%49	%50	%51	%MB
0	90.45	7.70	1.85	-
10500	66.50	22.57	10.87	-
14520	58.86	27.27	13.86	-
25920	42.07	37.93	19.99	-
31500	35.93	41.33	22.74	-
39900	28.25	45.39	26.35	100

Table 4-6. Relative Percent Composition Data for Thermolysis of **49** at 192.5°C.

Seconds	%**49**	%**50**	%**51**	%MB
0	90.47	7.57	1.96	-
2220.	80.67	13.64	5.68	-
5820.	67.18	21.83	11.01	-
8640.	57.38	27.97	14.65	-
11340.	50.76	32.06	17.17	100

Reaction of 9,10-Bis(trifluoroethenyl)phenanthrene (**40**) with CsF

9,10-Bis(trifluoroethenyl)phenanthrene (**40**, 0.0103 g, 3.05×10^{-5} mol) was dissolved in 2.0 ml of dry DMF to which was added 0.0113 g (7.43×10^{-5} mol) dry CsF. The reaction mixture was stirred rapidly for 2.5 hours at room temperature and a small aliquot of the reaction mixture was taken, diluted with water, extracted with diethyl ether, concentrated under a stream of N_2, then analyzed by analytical GLPC (Column: 0.125 inch x 10 feet, 20% QF-1 on Chromasorb WHP 100/120; Oven: constant at 205°C; Injector: 210°C) showing no reaction had occurred. The sample was then heated at 115°C. After 3.5 hours, an aliquot was taken as earlier and GLPC analysis shows three products with **40** approximately 70% consumed. Comparison with a **40** thermolysis reaction mixture sample (containing materials **40**, **41**, **49**, **50**, and **51**) shows that the CsF reaction has no products in common with the thermal reaction. After 19 hours further heating, GLPC analysis shows **40** has been consumed and one major and two minor products are observed. The reaction mixture was transferred to a separatory funnel with 50 ml of water and extracted with diethyl ether. The ether was then dried over anhydrous $MgSO_4$ and evaporated to

yield a small amount of brown oil. The oil was taken up in $CDCl_3$ and it's ^{19}F NMR spectrum observed. The spectrum shows two clusters of signals: -60 to -82 ppm (13 signals of various intensities) and -166 to -170 ppm (4 signals). Comparison of this spectrum with known spectra of **40** thermolysis products **41**, **49**, **50**, and **51** shows these two reactions have no products in common. No further characterization or separation was performed on the CsF reaction mixture.

Reaction of 4-Difluoromethylidene-3,3,5,5-tetrafluoro-1,2-(9,10-phenanthro)-cyclopent-1-ene (**50**) with Catalytic CsF

To an NMR sample in C_6D_6 with C_6F_6 internal standard containing 30.0% **49**, 44.6% **50**, and 25.4% **51** was added 20 µl of C_6D_6 containing traces of CsF. This fluoride spiked C_6D_6 solution was prepared by adding 2 ml of dry C_6D_6 to 10 mg of dry CsF then heating to reflux for 10 minutes. Visually, no CsF dissolved. The NMR sample was then flame sealed and placed in a Statim thermostated oil bath at 81°C for 57 minutes. After this time, the sample was cooled and found to contain 30.7% **49**, 19.7% **50**, and 49.5% **51** by integration of the ^{19}F NMR signals *versus* the C_6F_6 internal standard. The overall mass balance of **49**, **50**, and **51** *versus* the starting mixture is 95%.

Thermolysis of 1,2,2,3,3,4-hexafluoro-2,3-dihydrotriphenylene (**41**) Followed by GLPC

Two milligrams of a mixture being 62% **41** and 38% **51** was dissolved in 1.0 g of benzene and a small amount (a few mg) of phenanthrene was added as an internal standard. The solution was syringed into capillary tubes which were then flame sealed. The samples were placed in a Statim thermostated oil bath at 179.5°C. The progress of the reaction was followed by removing sealed samples over time and observing the reaction solution by analytical GLPC.

(Column: 0.125 inch x 10 feet, 20% QF-1 on Chromasorb WHP 100/120; Oven: constant at 205°C; Injector: 210°C) **41** decomposes and after 5.25 hours is 67% consumed. No new products were observed by GLPC of the reaction mixture, and there was no increase in the relative concentration of **51** over the thermolysis period. After 17 hours, **41** has been completely consumed, the **51** concentration has not changed, and there were no new products observed by GLPC.

Thermolysis of 1,2,2,3,3,4-Hexafluoro-2,3-dihydrotriphenylene (**41**) Followed by ^{19}F NMR

Three milligrams of a mixture being 85% **41** and 15% **51** was dissolved in 1.0 g of C_6D_6 containing traces of C_6F_6 as an internal standard. An aliquot of the solution was then transferred to an thick walled NMR tube and flame sealed under N_2. The sample was placed in a Statim thermostated oil bath at 179.5°C, taken out at specific time intervals and cooled rapidly in an ice-water bath, then observed by ^{19}F NMR. The sample's ^{19}F NMR spectrum was obtained five times over 799 minutes. The amount of **41** was clearly observed to decrease, and after 799 minutes, 32% of the **41** had been consumed. There were many new low intensity signals in the ^{19}F NMR spectrum observed in the region of -110 to -130 ppm. There was no change in the amount of **51**, and no **40**, **49**, nor **50** were observed to have formed. Disappearance of **41** (Ln(%**41**) *versus* time) did not follow first-order kinetics.

Solution Phase Photolysis of 1,2,2,3,3,4-Hexafluoro-2,3-dihydrotriphenylene (**41**)

A 0.003 g sample being 76.7% **41** and 23.3% **51**, was dissolved in 1.0 g of *n*-pentane containing traces of C_6H_5F. The solution was freeze-thaw degassed and an aliquot was syringed into a 5 mm quartz NMR tube and flame

sealed under N_2. The sample was photolyzed using a Rayonet reactor (model RPR-204, four low pressure mercury bulbs of type RUL 2537 Å from Southern N.E. Ultraviolet Co., Middleton, Connecticut) and the concentrations of all materials were monitored *versus* internal standard by ^{19}F NMR. (See Table 4-7 for data.) A fine film of insoluble solid was observed to have formed on the interior of the NMR tube. 1,4,5,5,6,6-Hexafluoro-2,3-(9,10-phenanthro)bicyclo[2.2.0]hex-2-ene (**61**) was observed in solution by ^{19}F NMR but not isolated due to the small amount of material.

1,4,5,5,6,6-Hexafluoro-2,3-(9,10-phenanthro)bicyclo[2.2.0]hex-2-ene (**61**): ^{19}F NMR (282 MHz, *n*-pentane, $CFCl_3$) -115.6 (dm, 2F, $^2J_{FF}$ = 213.7 Hz), -127.9 (dm, 2F, $^2J_{FF}$ = 213.7 Hz), -185.1 (bs, 2F)

Table 4-7. Relative Composition Data for Solution Phase Photolysis of **41**.

Minutes	%**41**	%**61**	%MB
0	100.	0	100.
61.	53.	28.	81.
114.	16.	22.	38.

Solution Phase Photolysis of 9,10-Bis(trifluoroethenyl)phenanthrene (**40**)

A sample consisting of 0.024 g (7.1×10^{-5} mol) **40** and 0.005 g (5×10^{-5} mol) C_6H_5F was dissolved in 1.5 ml of dry *n*-pentane and the solution was freeze-thaw degassed. The solution was syringed into an NMR tube and flame sealed under N_2 . The sample was irradiated by Rayonet reactor (model RPR-204, 4 low pressure mercury bulbs of type RUL 2537 Å from Southern N.E. Ultraviolet Co., Middleton, Connecticut) and the composition of the reaction mixture was monitored by ^{19}F NMR over a period of 21.6 hours. (See Table 4-8 for data.) After this time, the solution had turned clear light yellow from clear

colorless and a thin solid film had developed on the inside of the sample tube. Three materials identified earlier were seen in the reaction mixture; those being **41**, **49**, and **61**. Also observed in solution by ^{19}F NMR but not isolated was 1,4,5,5,6,6,-hexafluoro-2,3-(9,10-phenanthro)bicyclo[2.1.1]hex-2-ene (**60**).

1,4,5,5,6,6-hexafluoro-2,3-(9,10-phenanthro)bicyclo[2.1.1]hexene (**60**): ^{19}F NMR (282 MHz, *n*-pentane, $CFCl_3$) -115.3 (dtt, 2F, $^2J_{FF}$ = 162.7 Hz, $^3J_{FF}$ = 34.3 Hz, $^4J_{FF}$ = 7.3 Hz), -140.5 (dtt, 2F, $^2J_{FF}$ = 162.7 Hz, $^3J_{FF}$ = 34.3 Hz, $^4J_{FF}$ = 7.3 Hz), -211.7 (p, 2F, $^4J_{FF}$ = 7.3 Hz)

Table 4-8. Relative Composition Data for Solution Phase Photolysis of 9,10-Bis(trifluoroethenyl)phenanthrene (**40**).

Minutes	%**40**	%**41**	%**49**	%**60**	%**61**	%MB
0.	100.	0	0	0	0	-
12.	98.8	1.2	Trace	Trace	Trace	-
37.	97.3	2.7	Trace	Trace	Trace	-
87.	79.3	2.5	8.0	8.3	1.9	-
204.	58.0	2.8	20.7	14.8	3.6	-
281.	50.1	3.0	26.6	15.1	5.1	-
620.	27.1	1.4	42.4	24.0	5.2	-
1090.	13.8	1.4	50.3	28.9	5.5	-
1295.	7.8	1.3	53.6	27.2	6.0	89

An attempt to separate this resultant mixture was performed by preparative GLPC. (Column: 0.25 inch x 5 feet, 20% QF-1 on Chromasorb WHP 80/100; Oven: constant at 193°C; Injector: 200°C; TCD block: 212°C; He flow : 120 ml/minute.) Two fractions were isolated: Fraction 1, 5.3 mg light yellow solid, **49**

(54%), **50** (38%), **51** (8%); Fraction 2, 4.1 mg light yellow solid, **50** (6%), **41** (20%), **51** (74%).

Photolysis of 9,10-Bis(trifluoroethenyl)phenanthrene (**40**) and Thermolysis of Subsequent Reaction Mixture

A sample of **40** (0.021 g, 6.2×10^{-5} mol) was dissolved in 10 ml of dry, freeze-thaw degassed *n*-pentane and photolyzed with a Rayonet reactor (model RPR-204, 4 low pressure mercury bulbs of type RUL 2537 Å from Southern N.E. Ultraviolet Co., Middleton, Connecticut) through a Pyrex rotaflow tube for 21 hours and 45 minutes. After this time, the solution had turned from clear colorless to clear yellow with a fine film forming on the inside of the tube. The tube was then opened and the solvent removed under a stream of N_2. The remaining solid was dissolved in C_6D_6 and ^{19}F NMR shows at this time: **49** (47%), **60** (40%), **61** (13%). The sample was then flame sealed in a thick walled NMR tube. Heating this sample at 99°C for 1 hour effected no change. The sample was then heated at 184°C for 83 minutes. After this heating period, examining the reaction mixture by ^{19}F NMR showed: **49** (74%), **50** (3%), **41** (8%), **51** (15%) with no **60** or **61** remaining and no other new signals in the ^{19}F NMR spectrum. Internal standard was not used so the overall mass ballance from **40** was not established.

Preparation of Perfluoro-*E,Z,E*(and *E,E,E*)-4,5-dimethyl-2,4,6-octatriene (***Z*-56**(***E*-56**)

Perfluoro-*E,Z,E*(*E,E,E*)-4,5-dimethyl-2,4,6-octatriene (***Z*-56**(***E*-56**) was prepared by the method of Hansen.[70] A 100 ml, three necked, round bottom flask was assembled with two septa, a stopper, and a magnetic stirrer then flame dried under Ar purge. Dry, degassed DMF (25 ml) was syringed into the reaction vessel. Cd° powder (3.38 g, 3.00×10^{-2} mol) was weighed out into a

solid addition tube in a drybox then added to the reaction vessel. The mixture was cooled to 0°C, then 6.13 g (≈2.8 ml, $2.38x10^{-2}$ mol) perfluoro-*Z*-1-iodopropene[146] was added dropwise. The mixture was allowed to warm to RT and stirring was continued for 16 hours. Internal standard ^{19}F NMR at this time shows a 95% yield of *Z*-(XCd)FC=CF(CF_3) (where X = I and *Z*-CF=CF(CF_3) as a deep brown-red solution. Excess Cd° was removed by Schlenk filtering the solution into another three necked round bottom flask under Ar. Recrystallized CuBr (3.40 g, $2.37x10^{-2}$ mol) was weighed out into a solid addition tube in a drybox then added to the solution at RT. This mixture was stirred vigarously for 1 hour at RT, then the solids were removed by Schlenk filtering the solution into another three necked round bottom flask under Ar. A cold finger trap with a gas inlet port was added to the apparatus and 5.0 g ($3.08x10^{-2}$ mol) hexafluoro-2-butyne was slowly added from a tared Rotaflow tube over 10 minutes while maintaining the temperature of the system at RT by use of a water bath. This mixture was stirred vigarously at RT for 1 hour to yield a cloudy, orange-brown suspension. The condenser was removed and replaced with a vacuum takeoff. The reaction mixture was evacuated at 0.3 mm Hg and RT for 30 minutes and excess hexafluoro-2-butyne was trapped. Perfluoro-*Z*-1-iodopropene[146] (5.45 g, $2.11x10^{-2}$ mol) was then slowly added by syringe and the mixture stirred vigarously for 14 hours. When stirring was stopped, the mixture separated into an upper dark brown layer of DMF (majority of volume) and a clear colorless layer of perfluoroolefin on the bottom, with tan solid settling on the sides of the vessel. The mixture was then flash distilled using a bath temperature up to 60°C and vacuum of 1-2 mm Hg. Approximately 5 ml of clear, light yellow liquid was obtained with ≈1 ml of a dark yellow DMF layer on top. The bottom perfluoroolefin (**56**) layer was drawn out by syringe and transferred to a large, septum capped vial. The material was washed with 5 x 5 ml of cold water,

transferred to a new vial and dried over $MgSO_4$, then syringed through a 0.45 μm syringe filter into a vial containing activated 4 Å sieves. A 6.07 g (60%) sample of clear faint yellow **56** was obtained being 95% pure by GLPC.

Z-(XCd)FC=CF(CF_3) (X = I and *Z*-CF=CF(CF_3)): ^{19}F NMR (188MHz, DMF, $CFCl_3$) -65.7 (dd, 3 or 6 F, $^4J_{FF}$ = 22 Hz, $^3J_{FF}$ = 13 Hz), -141.3 (m, 1 or 2 F), -177.5 (dm, 1 or 2 F, $^3J_{FF}$ = 103 Hz)

Perfluoro-*E,Z,E*(*E,E,E*)-4,5-dimethyl-2,4,6-octatriene (***Z*-56**(***E*-56**): ^{19}F NMR (188 MHz, *n*-pentane, $CFCl_3$) *E,Z,E*: -60.3 (bs, 6F), -69.2 (dd overlapped with *E,E,E* triene signal, 6F, $^4J_{FF} \approx 19$ Hz, $^3J_{FF} \approx 10$ Hz), -139.8 (dq, 2F, $^3J_{FF}$ = 141.7 Hz, $^4J_{FF}$ = 19.2 Hz), -158.2 (dm overlapped with *E,E,E* triene signal, 2F, $^3J_{FF} \approx 141$ Hz), *E,E,E*: (pure sample obtained by preparative GLPC, after enrichment *via* photolysis of triene mixture through Pyrex) -63.1 (bs, 6F), -69.7 (dd, 6F, $^4J_{FF}$ = 20.2 Hz, $^3J_{FF}$ = 10.0 Hz), -136.3 (dq, 2F, $^3J_{FF}$ = 143.3 Hz, $^4J_{FF}$ = 20.2 Hz), -158.2 (dm, 2F, $^3J_{FF}$ = 143.3 Hz); UV in *n*-pentane, λ^{max} = 257nm, E^{max} = 1882.4 cm^2/mol; Low Resolution Mass Spectrum: m/z (% relative intensity) 424 (43), 336 (7), 317 (34), 286 (53), 267 (100), 217 (67); High Resolution Mass Spectrum: Calculated for $C_{10}F_{16}$ = 423.9744, Measured = 423.9741

Solution Phase Thermolysis of Perfluoro-*E,Z,E*(*E,E,E*)-4,5-dimethyl-2,4,6-octatriene (***Z*-56**(***E*-56**))

A 0.23 g (5.5×10^{-4} mol) sample of *E* and *Z* **56**was dissolved in 4.0 ml of dry *n*-pentane and 10 μl C_6H_5F added. The solution was freeze-thaw degassed and a 0.5 ml aliquot taken and transferred to a 5 mm, thick walled NMR tube (base rinsed, deionized water rinsed, acetone rinsed, flame dried) and flame sealed under N_2. The sample was then heated for a given time in a Statim thermostated oil bath and concentrations of all materials followed by integration of ^{19}F NMR signals *versus* internal standard C_6H_5F. (See Table 4-9 for data.)

Table 4-9. Relative Composition Data for Thermolysis of **56** at 154.5°C then 202.0°C.

Minutes	%*Z*-**56**	%*E*-**56**	%**59**	%MB
0	51.8	48.2	0	-
655.	41.6	58.4	0	-
895.	38.9	61.0	0	-
1795.	30.7	69.3	0	-
2145.	29.4	70.6	0	-
3057.	26.7	73.3	Trace	100
8822.	13.7	63.9	22.3	-

-Temperature was raised to 202.0°C and thermolysis continued-

9937.	6.3	54.7	38.9	-
10907.	5.6	51.9	42.5	-
15537.	6.0	54.0	40.4	-
19387.	5.3	56.8	37.8	95

Perfluoro-*cis*(and *trans*)-1,3,4-trimethyl-4-(*E*-1-propenyl)cyclobutene (**59**) were observed in the reaction solution by ^{19}F NMR and GLPC. (Column: 0.125 inch x 10 feet, 20% SE-30 on Chromasorb WHP 100/120; Oven: constant at 40°C; Injector: 120°C; N_2 flow: 20 ml/minute; Retention times: **56** 3.8 minutes, **59** 4.2 minutes).

Perfluoro-*cis*(and *trans*)-1,3,4-trimethyl-4-(*E*-1-propenyl)cyclobutene (**59**): ^{19}F NMR (188 MHz, *n*-pentane, C_6H_5F (-113.15)) -62.2 (bs, 3F), -63.3 (bs, 3F), -70.1 (bs, 6F), -119.5 (bs, 1F), -136.5 (dq, 1F, $^3J_{FF}$ = 144 Hz, $^4J_{FF}$ = 20 Hz), -144.5 (bs, 1F), -158.7 (dbs, 1F, $^3J_{FF}$ = 144 Hz)

Photolysis of Perfluoro-*E,Z,E*(*E,E,E*)-4,5-dimethyl-2,4,6-octatriene (***Z*-56**(***E*-56**)

A sample being 0.293 g (6.91×10^{-4} mol) **56** was dissolved in 4.0 ml of dry *n*-pentane and 10 µl C_6H_5F was added. The solution was freeze thaw degassed then a 0.5 ml aliquot was drawn and syringed into an 5 mm, Pyrex NMR tube (base rinsed, deionized water rinsed, acetone rinsed, flame dried), and the sample flame sealed under N_2. The photolysis was carried out by suspending the sample in a Rayonet reactor (model RPR-204, four low pressure mercury bulbs of type RUL 2537 Å from Southern N.E. Ultraviolet Co., Middleton, Connecticut) for a period of time then observing the reaction mixture by ^{19}F NMR. Relative concentrations of all species were obtained by integration *versus* internal standard C_6H_5F. (See Table 4-10 for data.)

Table 4-10. Relative Composition Data for Photolysis of Perfluoro-*E,Z,E*(*E,E,E*)-4,5-dimethyl-2,4,6-octatriene (***Z*-56**(***E*-56**).

Minutes	%***Z*-56**	%***E*-56**	%**62**	%**63**	%MB
0	53.7	46.3	0	0	-
255.	30.9	41.7	27.3	0	-
885.	5.0	27.9	58.4	8.6	-
2145.	0	2.0	80.0	18.0	90

For isolation of perfluoro-*trans*-2,3,5,6-tetramethyl-1,3-cyclohexadiene (**62**), a reaction solution after a suitable period of photolysis (composition being: 10% **56** (11 *E,E,E*:1 *E,Z,E*), 75% **62**, 15% perfluoro-*trans*-2,3,5,6-tetramethylbicyclo[2.2.0]hex-2-ene (**63**)) was frozen in liquid nitrogen and carefully thawed. This freeze-thaw cycle was repeated twice and resulted in phase seperation between the perfluoroorganics and *n*-pentane. While still cool (≈-50°C), the upper *n*-pentane layer could be syringed away containing

less than 3% perfluoroorganics by GLPC. The remaining perfluoroorganics (containing on average 10% or less *n*-pentane) were seperated by preparative GLPC. (Column: 0.25 inch x 12 feet, 20% SE-30 on Chromasorb P 60/80; Oven: constant at 60°C; Injector: 125°C; TCD block: 150°C, He flow: 20 ml/minute; Retention times: ***E*-56** 10.2 minutes (^{19}F NMR data for this material is given in perfluorotriene preparation experimental discussion), **62** 14.2 minutes).

Perfluoro-*trans*-2,3,5,6-tetramethyl-1,3-cyclohexadiene (**62**): ^{19}F NMR (188 MHz, *n*-pentane, C_6H_5F (-113.15)) -59.5 (m, 6F), -75.5 (m, 6F), -108.0 (m, 2F), -201.4 (m, 2F); UV in *n*-pentane, λ^{max} = 261 nm, E^{max} = 915.6 cm^2/mol; Low Resolution Mass Spectrum: m/z (% relative intensity) 424 (52), 336 (17), 317 (37), 267 (100); High Resolution Mass Spectrum: Calculated for $C_{10}F_{16}$ = 423.9744, Measured = 423.9746

Photolysis of Perfluoro-*trans*-2,3,5,6-tetramethyl-1,3-cyclohexadiene (**62**)

A solution being 10% **62** and 2% C_6H_5F was prepared in dry *n*-pentane and freeze-thaw degassed. An 0.5 ml aliquot was syringed into a 5 mm, quartz NMR tube which had been rinsed with base, deionized water, acetone, then flame dried under N_2 purge. The solution was then flame sealed under N_2. The sample was photolyzed using a Rayonet reactor (model RPR-204, four low pressure mercury bulbs of type RUL 2537 Å from Southern N.E. Ultraviolet Co., Middleton, Connecticut) and concentrations of all materials followed by integration of ^{19}F NMR signals *versus* internal standard C_6H_5F. (See Table 4-11 for data.)

Table 4-11. Relative Composition Data for Photolysis of Perfluoro-*trans*-2,3,5,6-tetramethyl-1,3-cyclohexadiene (**62**).

Minutes	%**62**	%**63**	%MB
0	100.0	0	100.
20.	93.5	6.5	98.
80.	73.4	26.6	95.
504.	27.9	72.1	71.
624.	25.6	74.4	58.

Perfluoro-*trans*-2,3,5,6-tetramethylbicyclo[2.2.0]hex-2-ene (**63**) was isolated out of the reaction solution after a suitable photolysis period. The solution was frozen in liquid nitrogen and carefully thawed. This freeze-thaw cycle was repeated twice and resulted in phase seperation between the perfluoroorganics and *n*-pentane. While still cool (≈-50°C), the upper *n*-pentane layer was carefully syringed away containing less than 3% perfluoroorganics by GLPC. The remaining perfluoroorganics (containing on average 10% or less *n*-pentane) were separated by preparative GLPC. (Column: 0.25 inch x 12 feet, 20% SE-30 on Chromasorb P 60/80; Oven: constant at 60°C; Injector: 125°C; TCD block: 130°C, He flow: 18 ml/minute; Retention times: **63** 7.1 minutes, **62** 8.6 minutes, *n*-pentane 9.2 minutes)

Perfluoro-*trans*-2,3,5,6-tetramethylbicyclo[2.2.0]hex-2-ene (**63**): ^{19}F NMR (188 MHz, $CHCl_3$, $CFCl_3$) -63.7 (bs, 3F), -64.2 (m, 3F), -73.2 (m, 3F), -75.9 (m, 3F), -174.4 (m 1F), -187.5 (m, 1F), -190.0 (m, 1F), -192.0 (dm, 1F, $J_{FF} \approx 15$ Hz); Low Resolution Mass Spectrum: m/z (% relative intensity) 424 (5), 336 (4), 317 (17), 286 (10), 151 (11), 119 (100), 113 (13); High Resolution Mass Spectrum: Calculated for $C_{10}F_{16}$ = 423.9744, Measured = 423.9749

Preparation of 4-[(Tetrahydro-2*H*-pyran-2-yl)oxy]-1-butanol

4-[(Tetrahydro-2*H*-pyran-2-yl)oxy]-1-butanol was prepared by the method of Hoffmann and Rabe.[133] 1,4-Butanediol (60.0 ml, 0.68 mol) was placed in a round bottom flask equipped with a strong magnetic stirrer. Diethyl ether (50 ml) and 5 drops of concentrated HCl were then added. 3,4-Dihydro-2H-pyran (DHP, 41.1 ml, 37.9 g, 0.45 mol) was dissolved in 50 ml diethyl ether and added dropwise at RT with rapid stirring to the heterogenous diol/ether mixture. The reaction mixture became homogenous after addition of approximately 10 ml of the DHP/ether solution. Upon completion of addition of the DHP solution, the reaction mixture was stirred for 3 hours at RT then extracted with 2 x 50 ml 10% aqueous KOH. The aqueous solution was back extracted with 50 ml diethyl ether then the ether extracts were combined and dried over $MgSO_4$. The ether was then removed by rotary evaporator and the remaining clear, colorless liquid was fractionally distilled through an 12 cm vigeraux column. 4-[(Tetrahydro-2*H*-pyran-2-yl)oxy]-1-butanol (52.8 g, 67%) was obtained as an early fraction boiling 100-109°C at 0.1 mm Hg as a colorless, viscous liquid.

4-[(Tetrahydro-2*H*-pyran-2-yl)oxy]-1-butanol: ^1H (200 MHz, $CDCl_3$, TMS) 1.45-1.85 (m, 10H), 3.22 (s, 1H), 3.37-3.95 (m, 6H), 4.60 (t, 1H, $^3J_{HH} \approx 3$ Hz); ^{13}C (50 MHz, $CDCl_3$, $CHCl_3$) 19.3, 25.2, 26.1, 29.6, 30.4, 62.0, 62.1, 67.2, 98.6

Preparation of 4-[(Tetrahydro-2*H*-pyran-2-yl)oxy]-1-butanal (**132**)

4-[(Tetrahydro-2*H*-pyran-2-yl)oxy]-1-butanal (**132**) was prepared by adaptation of a procedure as described by Corey and Schmidt.[147] A 1 L round bottom flask was flame dried under Ar purge and equipped with a strong magnetic stirrer and septum. 4-[(Tetrahydro-2*H*-pyran-2-yl)oxy]-1-butanol (17.9 g, 1.03×10^{-3} mol) was syringed into the flask followed by 400 ml of dry CH_2Cl_2. Pyridinium dichromate (PDC, 58.3 g, 1.55×10^{-1} mol) was quickly added and

rapid stirring begun. The solution turned dark brown-black within minutes of addition of the PDC. Stirring was continued for 15 hours at RT, then the reaction mixture was diluted with 400 ml diethyl ether. The black solid residue was gravity filtered and the resultant brown-black solution filtered through a bed of 150 mesh, basic activated (Brockmann I), aluminum oxide. The resultant solution was concentrated by rotary evaporator to yield a clear, colorless, slightly viscous liquid. This material was fractionally distilled through a 6 cm vigeraux column and 12.7 g (72%) clear, colorless, pleasant smelling **132** was obtained in an early fraction boiling 85-90°C at 0.05 mm Hg.

4-[(Tetrahydro-2*H*-pyran-2-yl)oxy]-1-butanal (**132**): ^{1}H (200 MHz, $CDCl_3$, TMS) 1.45-1.85 (m, 6H), 1.94 (p, 2H, $^{2}J_{HH}$ = 6.7 Hz), 2.54 (dt, 2H, $^{3}J_{HH}$ = 7.0 Hz, $^{3}J_{HH}$ = 1.7 Hz), 3.35-3.55 (m, 2H), 3.73-3.88 (m, 2H), 4.56 (t, 1H, $^{3}J_{HH} \approx$ 3 Hz), 9.78 (t, 1H, $^{3}J_{HH}$ = 1.7 Hz); ^{13}C (50 MHz, $CDCl_3$, $CHCl_3$) 19.5, 22.7, 25.5, 30.6, 41.1, 62.2, 66.4, 98.8, 202.2

Preparation of 5-[(Tetrahydro-2*H*-pyran-2-yl)oxy]-1,1-difluoropent-1-ene (**133**)

5-[(Tetrahydro-2*H*-pyran-2-yl)oxy]-1,1-difluoropent-1-ene (**133**) was prepared by adaptation of a procedure as described by Naae and Burton.[134] A three neck, 1 L flask was assembled under Ar purge with a mechanical stirrer, septum, and two addition funnels. The system was then flame dried under Ar purge. Dibromodifluoromethane (29.1 g, 1.39×10^{-1} mol) was transferred to a Rotaflow tube, dissolved in 60 ml of dry THF, then syringed into the reaction vessel followed by an additional 160 ml of dry THF. This solution was cooled to -5°C by an ice/salt bath. Dry THF (140 ml) was placed in an addition funnel followed by 50.0 ml (44.9 g, 2.75×10^{-1} mol) $P(N(CH_3)_2)_3$. Rapid stirring was begun and the $P(N(CH_3)_2)_3$ was added dropwise over 1 hour to the CF_2Br_2 solution with cooling. A fine white precipitate formed as addition continued.

Upon completing addition of the $P(N(CH_3)_2)_3$, the mixture was stirred at -5°C for 1 hour then brought to RT. 4-[(Tetrahydro-2H-pyran-2-yl)oxy]-1-butanal (**132**, 16.0 g, $9.29x10^{-2}$ mol) was dissolved in 50 ml of dry THF and placed in the second addition funnel. The **132** solution was then added to the ylide solution over 15 minutes at RT, then stirred for 16 hours at RT. At this time, the reaction mixture is a yellow-brown solution with a fine yellow precipitate settling on the bottom of the reaction vesel. The solids were gravity filtered and rinsed with 100 ml of diethyl ether. This solution was concentrated on a rotary evaporator to ≈25 ml volume which was taken up in 200 ml of fresh diethyl ether and exhaustively extracted with water. The ether solution was then dried over $MgSO_4$ and the ether removed by distillation up to 75°C at 115 mm Hg. 5-[(Tetrahydro-2*H*-pyran-2-yl)oxy]-1,1-difluoropent-1-ene (11.1 g, 58% by internal standard ^{19}F NMR; ≈80% pure, the remainder being ether and trace THF) was obtained as a clear, light brown liquid.

5-[(Tetrahydro-2*H*-pyran-2-yl)oxy]-1,1-difluoropent-1-ene (**133**): ^1H (200 MHz, $CDCl_3$, TMS) 1.45-1.85 (m, 8H), 2.03-2.17 (m, 2H), 3.33-3.57 (m, 2H), 3.75-3.92 (m, 2H), 4.17 (dtd, 1H, $^3J_{transHF}$ = 25.2 Hz, $^3J_{HH}$ = 7.94 Hz, $^3J_{cisHF}$ = 2.54 Hz), 4.55 (t, 1H, $^3J_{HH}$ ≈ 3 Hz); ^{13}C (50 MHz, $CDCl_3$, $CHCl_3$) 18.9 (d, 1C, $^3J_{CF}$ = 4.3 Hz), 19.4, 25.3, 29.3 (t, 1C, $^4J_{CF}$ ≈ 2 Hz), 30.6, 62.1, 66.3, 77.6 (t, 1C, $^2J_{CF}$ = 21.2 Hz), 98.7, 156.2 (t, 1C, $^1J_{CF}$ = 283.9 Hz); ^{19}F (188 MHz, $CDCl_3$, $CFCl_3$) -89.8 (d, 1F, $^2J_{FF}$ = 48.4 Hz), -92.3 (dd, 1F, $^2J_{FF}$ = 48.4 Hz, $^3J_{HF}$ = 25.2 Hz)

Preparation of 5,5-Difluoro-4-penten-1-ol (**134**)

5-[(Tetrahydro-2*H*-pyran-2-yl)oxy]-1,1-difluoropent-1-ene (**133**) was deprotected to 5,5-difluoro-4-penten-1-ol (**134**) by adaptation of a procedure as described by Beier and Mundy.[148] 5-[(Tetrahydro-2*H*-pyran-2-yl)oxy]-1,1-difluoropent-1-ene (**133**, 11.1 g, $4.3x10^{-2}$ mol delivered (80% pure, impurities

being ether and trace THF)) was dissolved in 70 ml 1,4-butanediol. Acid activated Dowex 50 x 80-200 ion exchange resin (5.0 g) was added and the mixture stirred rapidly for 2.5 hours. The reaction was then flash distilled down to a pressure of 0.5 mm Hg. Approximately 2 ml of THF and ether was collected upon pump down of the system. The fraction boiling between 55 and 110°C (applied bath temperature) was collected to yield ≈5 ml clear, colorless liquid. Being slightly acidic, this material was distilled off of 2 g of dry $NaHCO_3$ to yield 4.37 g (83%) clear, colorless **134** distilling from 74-78°C at 115 mm Hg.

5,5-Difluoro-4-penten-1-ol (**134**): ^1H (200 MHz, $CDCl_3$, TMS) 1.63 (tt, 2H, $^3J_{HH}$ = 7.42 Hz, $^3J_{HH}$ = 6.36 Hz), 2.07 (m, 2H), 2.78 (bs, 1H), 3.62 (t, 2H, $^3J_{HH}$ = 6.34 Hz), 4.16 (dtd, 1H, $^3J_{transHF}$ = 25.38 Hz, $^3J_{HH}$ = 7.78 Hz, $^3J_{cisHF}$ = 2.54 Hz); ^{13}C (50 MHz, $CDCl_3$, $CHCl_3$) 18.5 (d, 1C, $^3J_{CF}$ = 4.2 Hz), 32.1 (t, 1C, $^4J_{CF}$ = 2.1 Hz), 61.6, 77.3 (t, 1C, $^2J_{CF}$ = 21.3 Hz), 156.3 (dd, 1C, $^1J_{CF}$ = 284.9 Hz, $^1J_{CF}$ = 285.1 Hz); ^{19}F (188 MHz, $CDCl_3$, $CFCl_3$) -89.6 (d, 1F, $^2J_{FF}$ = 48.6 Hz), -92.1 (dd, 1F, $^2J_{FF}$ = 48.6 Hz, $^3J_{transHF}$ = 25.5 Hz); Low Resolution Mass Spectrum: m/z (% relative intensity) 104 (100), 84 (16), 77 (69)

Preparation of 5,5-Difluoro-4-pentenal (**135**)

5,5-Difluoro-4-pentenal (**135**) was prepared by adaptation of a procedure as described by Corey and Schmidt.[147] A round bottom flask was flame dried under Ar purge and 150 ml of dry CH_2Cl_2 added. 5,5-Difluoro-4-penten-1-ol (**134**, 4.37 g, 3.58×10^{-2} mol) was then added followed by 20.17 g (5.36×10^{-2} mol) pyridinium dichromate. The reaction mixture was stirred at RT for 18 hours then dilluted with 250 ml diethyl ether. The mixture was then gravity filtered to remove the black solids which were rinsed with diethyl ether, then, the resultant brown-black solution was filtered through a bed of 150 mesh, base activated (Brockmann I) aluminum oxide. Contamination by pyridine was

detected by GLPC so the reaction solution was extracted with 2 x 50 ml half saturated $CuSO_4$, then 2 x 50 ml water. By GLPC, the pyridine had been removed, so the solution was dried over $MgSO_4$. The ether and CH_2Cl_2 were carefully distilled through a 6 cm vigeraux column and the remainder transferred to a micro distillation apparatus. As the heating bath temperature was raised to ≈40°C with an applied pressure of 100 mm Hg, the remainder of material bumped over. Due to the small amount of material, distillation was not attempted again. A clear, light yellow liquid was obtained being 87% pure **135** (3.37 g, 70%) contaminated with diethyl ether and CH_2Cl_2.

5,5-Difluoro-4-pentenal (**135**): ^1H (200 MHz, $CDCl_3$, TMS) 2.22-2.35 (m, 2H), 2.53 (tm, 2H, $^3J_{HH}$ = 6.92 Hz), 4.22 (dtd, 1H, $^3J_{transHF}$ = 25.10 Hz, $^3J_{HH}$ = 7.78 Hz, $^3J_{cisHF}$ = 2.38 Hz), 9.76 (t, 1H, $^3J_{HH}$ = 1.2 Hz); ^{13}C (50 MHz, $CDCl_3$, $CHCl_3$) 14.9 (d, 1C, $^3J_{CF}$ = 4.9 Hz), 43.0 (t, 1C, $^4J_{CF}$ = 2.6 Hz), 77.0 (t, 1C, $^2J_{CF}$ = 31.9 Hz), 156.2 (dd, 1C, $^1J_{CF}$ = 285.6 Hz, $^1J_{CF}$ = 286.2 Hz), 200.6; ^{19}F (188 MHz, $CDCl_3$, $CFCl_3$) -88.9 (d, 1F, $^2J_{FF}$ = 46.4 Hz, -91.0 (dd, 1F, $^2J_{FF}$ = 46.4 Hz, $^3J_{transHF}$ = 25.0 Hz); Low Resolution Mass Spectrum: m/z (% relative intensity) 120 (10), 100 (11), 91 (7), 77 (66), 69 (100), 64 (19); High Resolution Mass Spectrum: Calculated for $C_5H_6F_2O$ = 120.0386, Measured = 120.0356

Preparation of 1,1,6,6-Tetrafluoro-1,5-hexadiene (**123**)

1,1,6,6-Tetrafluoro-1,5-hexadiene (**123**) was prepared by adaptation of a procedure as described by Naae and Burton.[134] A three necked round bottom flask was assembled with two septa, a pressure equalizing addition funnel, magnetic stirrer, and flame dried under Ar purge. Dibromodifluoromethane (1.55 g, 7.39×10^{-3} mol) was transferred to a Rotaflow tube then dissolved in 15 ml of dry triglyme and added to the reaction vessel by syringe. This solution was cooled to -5°C with an ice/salt bath. $P(N(CH_3)_2)_3$ (2.6 ml, 2.3 g, 1.4×10^{-2}

mol) was dissolved in 10 ml of dry triglyme in the addition funnel, then added to the CF_2Br_2 solution over 15 minutes with good stirring and cooling at -5°C. The resultant cloudy solution, thick with white precipitate, was stirred for 1 hour at -5°C then brought to RT. 5,5-Difluoro-4-pentenal (**135**, 0.90 g, $7.5x10^{-3}$ mol) was dissolved in 5 ml dry triglyme and added to the ylide solution at RT over 5 minutes. This mixture was allowed to stir for 18 hours at RT. The reaction mixture was then flash distilled into a two necked Rotaflow trap up to a bath temperature of 40°C at 0.5 mm Hg. 1,1,6,6-Tetrafluoro-1,5-hexadiene (0.44 g, 38%) was obtained being a clear, colorless liquid containing traces of diethyl ether, CH_2Cl_2, and $OP(N(CH_3)_2)_3$.

1,1,6,6-Tetrafluoro-1,5-hexadiene (**123**): ^1H (300 MHz, $CDCl_3$, TMS) 2.05-2.08 (m, 4H), 4.06-4.20 (dm, 2H, $^3J_{transHF}$ = 25.5 Hz); ^{13}C (75 MHz, $CDCl_3$, $CHCl_3$) 22.3 (m, 2C), 76.8 (t, 2C, $^2J_{CF}$ = 21.5 HZ), 156.6 (dd, 2C, $^1J_{CF}$ = 285.6 Hz, $^1J_{CF}$ = 285.7 Hz); ^{19}F (282 MHz, $CDCl_3$, $CFCl_3$) -89.0 (d, 2F, $^2J_{FF}$ = 46.4 Hz, -91.2 (dd, 2F, $^2J_{FF}$ = 46.4 Hz, $^3J_{transHF}$ = 25.5 Hz); Low Resolution Mass Spectrum: m/z (% relative intensity) 154 (1), 134 (1), 115 (2), 95 (2), 85 (23), 77 (100), 64 (2); High Resolution Mass Spectrum: Calculated for $C_6H_6F_4$ = 154.0405, Measured = 154.0410

Gas Phase Thermolysis of 1,1,6,6-Tetrafluoro-1,5-hexadiene (**123**)

An ≈100 mg sample of **123** was obtained 98% pure by preparative GLPC seperation from an NMR solution in C_6D_6. (Column: 0.25 inch x 12 feet, 20% SE-30 on Chromosorb P 80/100; Oven: constant at 80°C; Injector: 100°C; TCD block: 110°C; He flow rate: 35 ml/minute) Eight millimeter Hg samples of **123** were expanded into the gas kinetics vessel as described in Appendix A, and conversion to 3,3,4,4-tetrafluoro-1,5-hexadiene (**124**) followed by GLPC. (See Table 4-12 for data, Column: 0.125 inch x 15 feet, $AgNO_3/C_6H_5CH_2CN$

30% on Chromosorb Z 80/100; Oven: constant at 35°C; N_2 flow rate: 30 ml/minute; Retention times: **124** 5.9 minutes, **123** 7.0 minutes) Following the gas phase reaction *versus* internal standard *n*-octane showed the yield of this transformation to be 99%. Reversibility of **124** back to **123** was not observed.

Isolation of **124:** A 30% solution of **123** in C_6H_6 was sealed in a Carius tube and thermolyzed at 185°C for 42 hours. ^{19}F NMR at this time shows only **124**. Pure **124** was isolated by preparative scale GLPC from this solution. (Column: 0.25 inch x 20 feet, 20% Triton X-305 on Chromosorb W 80/100; Oven: 90°C constant ; Injector: 120°C; TCD block: 120°C; He flow rate: 30 ml/minute)

3,3,4,4-Tetrafluoro-1,5-hexadiene (**124**): ^1H (300 MHz, $CDCl_3$, TMS) 5.66-5.72 (m, 1H), 5.81-6.08 (m, 2H); ^{13}C (75 MHz, $CDCl_3$, $CHCl_3$) 114.9 (tt, 1C, $^1J_{CF}$ = 247.1 Hz, $^2J_{CF}$ = 35.7 Hz), 124.0 (m, 1C), 126.5 (t, 1C, $^2J_{CF}$ = 24.6 Hz); ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$) -115.6 (dm, 4F, $^3J_{HF}$ = 12.1 Hz); Low Resolution Mass Spectrum: m/z (% relative intensity) 154 (1), 135 (5), 134 (2), 115 (8), 85 (13), 78 (3), 77 (100), 57 (3), 51 (16); High Resolution Mass Spectrum: Calculated for $C_6H_6F_4$ = 154.0405, Measured = 154.0400

Preparation of 4-Methylidene-1-cyclohexanone ethylene ketal (**137**)

4-Methylidene-1-cyclohexanone ethylene ketal (**137**) was prepared by adaptation of a general procedure.[135] A 250 ml, three necked, round bottom flask was assembled with a magnetic stirrer, two pressure equalizing addition funnels, and a septum. The system was then flame dried under Ar purge. $(C_6H_5)_3PCH_3Br$ (22.6 g, $6.33x10^{-2}$ mol) was added and a slurry created by the addition of 80 ml of dry THF. This slurry was cooled to 0°C by an ice-water bath. *n*-Butyl lithium (*n*-BuLi) in *n*-pentane (31.7 ml of a 2.0 M solution, $6.34x10^{-2}$ mol)

Table 4-12. Averaged Percent Composition Data for Thermolysis of **123**.

207.2°C

Seconds	%123
2100	95.2
3600	92.1
5760	87.7
8220	82.9
12120	75.9
15840	69.9
18000	66.7

216.2°C

Seconds	%123
1800	92.7
3600	86.0
5400	79.2
7200	74.1
9000	69.4
10800	63.9
14700	54.2

224.2°C

Seconds	%123
1800	88.0
3720	76.3
5460	68.2
7200	60.6
9000	53.7
10800	47.0

228.8°C

Seconds	%123
1500	86.9
3000	74.8
4500	66.4
5400	61.2
6600	55.0
8100	48.1

235.7°C

Seconds	%123
1200	84.1
2520	69.6
3600	60.4
4860	50.8
6000	43.5
7200	36.9

241.6°C

Seconds	%123
900	82.9
1800	69.7
2700	58.2
3600	48.8
4500	41.0
5400	34.0

was added to an addition funnel with a Teflon stopcock. While vigarously stirring the slurry, the *n*-BuLi solution was added over 40 minutes. The solution turned canary yellow upon addition of *n*-BuLi. At 30 minutes into the addition, the mixture had become a clear, deep yellow-red homogenous solution. Upon completion of addition of the *n*-BuLi, the solution was warmed to RT and stirred for 1 hour. The ylide solution was then cooled to 5°C and 9.0 g (5.76×10^{-2} mol)

1,4-cyclohexanedione mono-ethylene ketal in 20 ml dry THF was added dropwise from the second addition funnel over 20 minutes. The reaction mixture was then stirred at RT for 15 hours to yield a clear, light yellow solution containing much fine white precipitate. Water (3 ml) was then added to decompose any possible remaining ylide. The solids were gravity filtered and rinsed with 40 ml THF and 50 ml hexanes. The solution was then concentrated by rotary evaporator to yield an oil with some white solid. This material was then dissolved in 100 ml methanol and extracted with 3 x 100 ml hexanes. The combined hexanes where then extracted with 3 x 100 ml saturated aqueous NaCl. The hexane solution was then dried over $MgSO_4$ and concentrated by rotary evaporator to yield ≈5 ml of clear oil containing some white crystals. This material was dissolved in 25 ml hexanes and set aside in a freezer at -5°C for 18 hours. The solution was vacuum filtered (while cold) through a fritted filter to remove the white crystalline $OP(C_6H_5)_3$. The resultant clear, colorless solution was concentrated by rotary evaporator to yield 6.2 g (69%) clear, colorless **137**.

4-Methylidene-1-cyclohexanone ethylene ketal (**137**): ^1H (200 MHz, $CDCl_3$, TMS) 1.69 (t, 4H, $^3J_{HH}$ = 6.2 Hz), 2.27 (t, 4H, $^3J_{HH}$ = 6.2 Hz), 3.96 (s, 4H), 4.66 (s, 1H); ^{13}C (50 MHz, $CDCl_3$, $CHCl_3$) 31.9, 35.8, 64.2, 108.1, 108.5, 147.2

Preparation of 4-Methylidenecyclohexanone (**138**)

4-Methylidenecyclohexanone (**138**) was prepared by adaptation of a procedure as described by Huet *et al.*[136] Silica gel (73 g) was suspended in 180 ml of CH_2Cl_2 by rapid stirring in a round bottom flask. Sulfuric acid (15%, 7.3 g) was added to the silica gel slurry dropwise. After 5 minutes, the beads of aqueous acid had been adsorbed onto the silica gel. 4-Methylidene-1-cyclohexanone ethylene ketal (**137**, 6.2 g, 4.0×10^{-2} mol) was then added and rapid stirring continued. After 3 hours, GLPC analysis shows a 4:1 ratio of

deprotected to protected ketone. The solution was filtered, then subjected to a second treatment as above (38 g silica gel, 4.8 g of 15% H_2SO_4). After 3 hours stirring, GLPC analysis shows 10.2:1 ratio of **138**:**137**. The solution was then filtered and the silica gel rinsed with 2 x 100 ml CH_2Cl_2 and then concentrated by rotary evaporator to yield 4.6 g of light yellow oil. This material was distilled yielding and inital fraction of CH_2Cl_2 followed by 3.9 g (90%) clear, colorless **138** boiling from 99-102°C at 115 mm Hg.

4-Methylidenecyclohexanone (**138**): ^1H (200 MHz, $CDCl_3$, TMS) 2.35-2.60 (m, 8H), 4.89 (s, 2H); ^{13}C (50 MHz, $CDCl_3$, $CHCl_3$) 32.9, 41.4, 110.5, 144.2, 210.3

Preparation of 1-Difluoromethylidene-4-methylidenecyclohexane (**128**)

1-Difluoromethylidene-4-methylidenecyclohexane (**128**) was prepared by adaptation of a procedure as described by Naae and Burton.[134] A 250 ml, three necked, round bottom flask was equipped with a septum, pressure equalizing addition funnel, and strong magnetic stirrer. The system was then flame dried under Ar purge. Dibromodifluoromethane (5.8 g, $2.8x10^{-2}$ mol) was weighed out into a Rotaflow tube, dissolved in 75 ml dry THF, then transferred to the reaction vessel by syringe. This solution was cooled to -5°C. $P(N(CH_3)_2)_3$ (10.2 ml, 9.1 g, $5.6x10^{-2}$ mol) was transferred to the addition funnel and dissolved in 40 ml of dry THF then added to the CF_2Br_2 solution dropwise over 30 minutes with cooling. The resultant slurry of white precipitate was stirred 1 hour then brought to RT. 4-Methylidenecyclohexanone (**138**, 1.92 g, $1.74x10^{-2}$ mol) was dissolved in 5 ml dry THF and added dropwise to the ylide solution. This mixture was stirred for 14 hours at RT. The yellow solid was gravity filtered and the solution concentrated to ≈10 ml volume by simple distillation. The liquid was then dissolved in 200 ml diethyl ether and exhaustively extracted

with water. This ether solution was then dried over $MgSO_4$, filtered, and distilled off through a 6 cm vigeraux column. The remainder of the material was transferred to a micro distillation apparatus and distilled under vacuum to yield 1.5 g (60%) **128** as an end fraction boiling 55-59°C at 115 mm Hg.

1-Difluoromethylidene-4-methylidenecyclohexane (**128**): ^1H (300 MHz, $CDCl_3$, TMS) 2.18 (m, 8H), 4.70 (s, 2H); ^{13}C (50 MHz, $CDCl_3$, $CHCl_3$) 25.5, 34.4 (t, 2C, $^3J_{CF} \approx 2$ Hz), 87.1 (t, 1C, $^2J_{CF} = 18.9$ Hz), 108.6, 147.3, 150.9 (t, 1C, $^1J_{CF} = 279.5$ Hz); ^{19}F (282 MHz, $CDCl_3$, $CFCl_3$) -98.4 (m, 2F); Low Resolution Mass Spectrum: m/z (% relative intensity) 144 (100), 129 (65), 127 (12), 115 (20), 109 (40), 97 (9), 79 (15), 77 (18); High Resolution Mass Spectrum: Calculated for $C_8H_{10}F_2$ = 144.0750, Measured = 144.0753

Gas Phase Thermolysis of 1-Difluoromethylidene-4-methylidenecyclohexane (**128**)

An ≈100 mg sample of **128** was obtained 99% pure by preparative GLPC. (Column: 0.25 inch x 12 feet, 20% SE-30 on Chromosorb P 80/100; Oven: constant at 145°C; Injector: 175°C; TCD block: 170°C; He flow rate: 30 ml/minute) Eight millimeter Hg samples of **128** were expanded into the gas kinetics vessel as described in Appendix A, and conversion to 1,1-difluoro-2,5-dimethylidenecyclohexane (**139**) followed by GLPC. (See Table 4-13 for data, Column: 0.125 inch x 11.5 feet, 20% DNP on Chromosorb WHP 60/80; Oven: constant at 140°C; N_2 flow rate: 30 ml/minute; Retention times: **128** 5.3 minutes; **139** 7.3 minutes) Following the gas phase reaction *versus* internal standard *n*-octane showed the yield of this transformation to be 98%. Reversibility of **139** back to **128** was not observed. 1,1-Difluoro-2,5-dimethylidenecyclohexane (**139**) was isolated by twice thermolyzing 12 mm Hg samples of **128** in both

thermolysis vessels for 150 minutes at 332.6°C and collecting the product in a Rotaflow tube for analysis.

1,1-Difluoro-2,5-dimethylidenecyclohexane (**139**): ^{1}H (300 MHz, $CDCl_3$, TMS) 2.25-2.30 (m, 2H), 2.36-2.41 (m 2H), 2.67 (tt, 2H, $^{3}J_{HF}$ = 13.7 Hz, $^{4}J_{HH}$ = 1.2Hz), 4.87 (m, 1H), 4.92 (m, 1H), 5.09 (m, 1H), 5.39 (m, 1H); ^{19}F (282 MHz, $CDCl_3$, $CFCl_3$) -100.9 (t, 2F, $^{3}J_{HF}$ = 13.7 Hz); Low Resolution Mass Spectrum: m/z (% relative intensity) 144 (100), 129 (88), 115 (27), 109 (86), 97 (29); High Resolution Mass Spectrum: Calculated for $C_8H_{10}F_2$ = 144.0750, Measured = 144.0748

Table 4-13. Averaged Percent Composition Data for Thermolysis of **128**.

279.9°C

Seconds	**128**
2400	90.8
4500	84.3
6120	79.4
7980	73.4
14880	58.3
21000	44.5

287.8°C

Seconds	**128**
1260	91.8
2460	85.1
3480	79.3
4800	72.5
6180	66.9
9180	54.8
13860	39.6
19920	26.2

292.1°C

Seconds	**128**
1500	87.5
3060	75.4
5280	62.7
7320	52.0
9240	43.8
11940	36.0
14880	25.9

Table 4-13 - Continued-

297.6°C	
Seconds	**128**
1200	87.2
2880	70.2
4620	56.4
6000	47.1
11160	23.6
13740	18.0
16380	13.3

303.0°C	
Seconds	**128**
600	89.9
1440	77.4
2100	68.8
2760	61.4
4620	44.7
8340	22.3
10200	15.6

309.1°C	
Seconds	**128**
600	85.8
1320	71.4
1920	60.7
2520	51.8
3120	43.4
3720	38.0
10680	6.4

Preparation of 1,4-Di(difluoromethylidene)cyclohexane (**129**)

1,4-Di(difluoromethylidene)cyclohexane (**129**) was prepared by adaptation of a procedure as described by Naae and Burton.[134] A 500 ml, three necked, round bottom flask was equipped with a mechanical stirrer, septum and pressure equalizing addition funnel and flame dried under Ar purge. Dibromodifluoromethane (16.93 g, 8.07×10^{-2} mol) was transferred to a Rotaflow tube then dissolved in 70 ml of dry THF. This solution was transferred to the reaction vessel by syringe followed by an additional 70 ml dry THF. $P(N(CH_3)_2)_3$ (29.5 ml, 26.5 g, 1.62×10^{-1} mol) was dissolved in 90 ml dry THF in the addition funnel. The CF_2Br_2 solution was cooled to -5°C with an ice/salt bath then the $P(N(CH_3)_2)_3$ solution was added dropwise over 1 hour. This mixture was stirred at -5°C for 2 hours then brought to RT. 1,4-Cyclohexanedione (4.5 g, 4.0×10^{-2} mol) was dissolved in 40 ml dry THF and added to the ylide solution over 35 minutes. The reaction mixture was then stirred for 18 hours at RT. The pale yellow solids were then filtered away from

the yellow-brown solution. The solution was then concentrated by rotary evaporator down to a volume of ≈15 ml which was taken up in 200 ml diethyl ether. The ether solution was exhaustively extracted with water then dried over $MgSO_4$. The ether was distilled off through a 6 cm vigeraux column to leave ≈3 ml of clear brown liquid. This material was transferred to a micro distillation apparatus and vacuum applied down to 15 mm Hg and ≈1 ml of ether frothed over. As a later fraction, 2.5 g (36%) clear, light yellow **129** was obtained boiling 60-62°C at a pressure of 12-10 mm Hg.

1,4-Di(difluoromethylidene)cyclohexane (**129**): ^1H (300 MHz, $CDCl_3$, TMS) 2.15 (p, 8H, $^4J_{HF} \approx 1.3$ Hz); ^{13}C (75 MHz, $CDCl_3$, $CHCl_3$) 23.9 (m, 4C), 86.5 (t, 2C, $^2J_{CF} = 19.2$ Hz), 151.2 (t, 2C, $^1J_{CF} \approx 280.2$ Hz); ^{19}F (282 MHz, $CDCl_3$, $CFCl_3$) -97.7 (septet, 4F, $^4J_{HF} \approx 1.3$Hz); Low Resolution Mass Spectrum: m/z (% relative intensity) 180 (100), 165 (12), 145 (19), 127 (15), 111 (61), 109 (26), 103 (19), 77 (24); High Resolution Mass Spectrum: Calculated for $C_8H_8F_4$ = 180.0562, Measured = 180.0571

Gas Phase Thermolysis of 1,4-Di(difluoromethylidene)cyclohexane (**129**)

An ≈100 mg sample of **129** was obtained 99% pure by preparative GLPC seperation from a solution in THF. (Column: 0.25 inch x 12 feet, 20% SE-30 on Chromosorb P 80/100; Oven: constant at 130°C; Injector: 150°C; TCD block: 150°C; He flow rate: 30 ml/minute) Eight millimeter Hg samples of **129** were expanded into the gas kinetics vessel as described in Appendix A, and conversion to 1,1,2,2-tetrafluoro-3,6-dimethylidenecyclohexane (**141**) followed by GLPC. (See Table 4-14 for data, Column: 0.125 inch x 10 feet, 20% QF-1 on Chromosorb WHP 100/120; Oven: constant at 110°C; N_2 flow rate: 30 ml/minute; Retention times: **129** 3.4 minutes, **141** 5.1 minutes) Following the reaction *versus* internal standard (*n*-octane) showed the yield of this

Table 4-14. Averaged Percent Composition Data for Thermolysis of **129**

329.2°C	
Seconds	**129**
1200	85.6
2400	72.5
3600	61.8
4920	51.6
6000	45.4
7200	37.7

336.9°C	
Seconds	**129**
2280	67.7
6000	31.5
8460	17.7
10980	10.2
16860	3.4

343.2°C	
Seconds	**129**
1680	59.8
2700	43.6
3960	30.0
5160	21.2
6360	14.4
7560	10.3

349.1°C	
Seconds	**129**
960	66.6
1800	49.1
2700	31.5
3840	20.0
4800	13.5
6600	7.1

354.5°C	
Seconds	**129**
780	66.0
1200	51.0
1500	42.5
1920	35.1
2340	26.8
2760	22.4

359.8°C	
Seconds	**129**
600	65.6
1200	40.6
1800	26.4
2400	16.7
3000	11.1

transformation to be 99%. Reversibility of **141** back to **129** was not observed. The product **141** was isolated by twice thermolyzing 12 mm Hg samples of **129** in both thermolysis vessels for 200 minutes at 359.8°C and collecting the product in a Rotaflow tube for analysis.

1,1,2,2-Tetrafluoro-3,6-dimethylidenecyclohexane (**141**): ^{1}H (300 MHz, $CDCl_3$, TMS) 2.42 (bs, 4H), 5.35 (s, 1H), 5.63 (s, 1H); ^{19}F (282 MHz, $CDCl_3$, $CFCl_3$) -123.1 (s, 4F); Low Resolution Mass Spectrum: m/z (% relative intensity)

180 (60), 165 (17), 145 (19), 111 (100), 77 (23); High Resolution Mass Spectrum: Calculated for $C_8H_8F_4$ = 180.0562, Measured = 180.0564

Preparation of 2-(2-Oxocyclopentyl)cyclopentanone (**143**)

2-(2-Oxocyclopentyl)cyclopentanone (**143**) was prepared by the method of Paul.[137] A three necked, round bottom flask was equipped with a condenser, magnetic stirrer, and pressure equalizing addition funnel then flame dried under Ar purge. Freshly cut sodium metal (0.75 g, $3.3x10^{-2}$ mol) was placed in the flask followed by 20 ml of dry toluene. The system was heated to reflux and stirred rapidly, breaking the Na° into small spheres. Ethyl-2-oxocyclopentane carboxylate (5.0 g, $3.2x10^{-2}$ mol) was dissolved in 5 ml of toluene and added dropwise to the Na° at reflux with rapid stirring. Upon completion of addition, the mixture was heated at reflux for 1 hour, after which all of the Na° metal had been consumed. 2-Chlorocyclopentanone (3.97 g, $3.34x10^{-2}$ mol) was dissolved in 5 ml dry toluene and added dropwise to the refluxing enolate solution. Upon completion of addition, the mixture was held at a gentle reflux for 9 hours. The resultant solids were then gravity filtered and the reaction solution extracted with 3 x 50 ml of water, then dried over $MgSO_4$. The toluene was then removed by rotary evaporator to yield 3.4 g (66%) crude product which was purified by Kughelrohr distillation to give 2.4 g (47%) pure white solid ethyl 2,2´-bismethylenecyclopentane-2-carboxylate. This material was added to a round bottom flask containing 15 ml of 20% HCl and assembled with a condenser. The mixture was brought to a gentle reflux and ethanol was added (≈3 ml) until the mixture became homogenous. The solution was heated at a gentle reflux for 24 hours at which time GLPC analysis showed the decarboxylation to be ≈90% complete. The reaction solution was extracted with 4 x 50 ml diethyl ether and the ether solution was exhaustively extracted with

water then dried over MgSO4. The ether was removed by rotary evaporator and the resultant material purified by Kughelrohr distillation to yield 0.91 g (55%) solid, white, **143**.

2-(2-Oxocyclopentyl)cyclopentanone (**143**): ^{1}H NMR (300 MHz, $CDCl_3$, TMS) 1.52-1.88 (m, $4H_{meso\ and\ d,l}$), 1.98-2.39 (m, $8H_{meso\ and\ d,l}$), 2.53 (t, $2H_{meso\ or\ d,l}$, $^{3}J_{HH} \approx 8.9$ Hz), 2.63 (t, $2H_{meso\ or\ d,l}$, $^{3}J_{HH} \approx 9.1$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$, $CDCl_3$) *meso* and *d,l* diasteromers: 20.2, 20.4, 24.9, 26.3, 37.4, 37.6, 48.0, 48.7, 218.3, 219.2

Preparation of *meso* and *d,l*-1-(2-Difluoromethylidenecyclopentyl)-2-difluoromethylidenecyclopentane (***meso*-131**,***d,l*-131**)

meso and *d,l*-1-(2-Difluoromethylidenecyclopentyl)-2-difluoromethylidenecyclopentane (***meso*-131**,***d,l*-131**) was prepared by adaptation of a procedure as described by Naae and Burton.[134] A 500 ml, three necked, round bottom flask was equipped with a mechanical stirrer, pressure equalizing addition funnel, septum, and flame dried under Ar purge. Dibromodifluoromethane (21.25 g, 1.01×10^{-1} mol) was transferred to a Rotaflow tube, dissolved in 80 ml dry THF, then syringed into the reaction vessel followed by 150 ml dry THF. The CF_2Br_2 solution was then cooled to -5°C. $P(N(CH_3)_2)_3$ (36.0 ml, 32.3 g, 1.98×10^{-1} mol) was transferred to the addition funnel and dissolved in 100 ml dry THF. This solution was added dropwise to the CF_2Br_2 with cooling over 1.75 hours. The resultant slurry of white solid was stirred at -5°C for 1.33 hours after which it was heated to 40°C. 2-(2-Oxocyclopentyl)cyclopentanone (**143**, 4.27 g, 2.57×10^{-2} mol) was dissolved in 20 ml dry THF and added dropwise to the ylide mixture at 40°C over 1 hour with vigorous stirring. The mixture was then stirred for 17 hours at 40°C. At this time, the yield of **131** is 31%, as checked by ^{19}F NMR *versus* added C_6H_5F. The

resultant reaction mixture was gravity filtered to remove the tan solids and the solution concentrated by rotary evaporator to yield ≈3 ml of dark brown viscous liquid. Diethyl ether (250 ml) was added and this solution exhaustively extracted with water. The ether phase was then dried over $MgSO_4$, and concentrated by rotary evaporator to yield 1.9 g (28%) light brown oil being 90% **131**, 8% THF/diethyl ether, and 2% $OP(N(CH_3)_2)_3$.

meso and *d,l*-1-(2-Difluoromethylidenecyclopentyl)-2-difluoromethylidenecyclopentane (***meso*-131**,***d,l*-131**): ^1H NMR (200 MHz, $CDCl_3$, TMS) 1.43-1.86 (m, $8H_{meso \text{ and } d,l}$), 2.12-2.40 (m, $4H_{meso \text{ and } d,l}$), 2.78 (bs, $2H_{3° CH, meso}$), 2.96 (bs, $2H_{3° CH, d,l}$); ^{19}F NMR (188 MHz, $CDCl_3$, $CFCl_3$) -91.1 (d, $1F_{d,l}$, $^2J_{FF}$ = 63.0 Hz), -91.2 (d, $1F_{meso}$, $^2J_{FF}$ = 61.6 Hz), -91.5 (d, $1F_{meso}$, $^2J_{FF}$ = 61.6 Hz), -92.8 (d, $1F_{d,l}$, $^2J_{FF}$ = 63.0 Hz); ^{13}C NMR (50 MHz, $CHCl_3$, TMS) *meso* and *d,l* diasteromers: 23.9, 24.6, 26.0, 26.6, 29.3, 30.9, 41.0 (m, C), 93.0 (t, C, $^2J_{CF}$ = 19.2 Hz), 151.2 (t, C, $^1J_{CF}$ = 280.9 Hz); Low Resolution Mass Spectrum: m/z (relative intensity): *meso*: 234 (21), 214 (6), 118 (7), 117 (100), 116 (12), 115 (5), 97 (23), 77 (7); *d,l*: 234 (30), 214 (4), 118 (7), 117 (100), 116 (12), 115 (5), 97 (22), 77 (4); High Resolution Mass Spectrum: Calculated for $C_{12}H_{14}F_4$ = 234.103, Measured (*d,l*) =234.104, Measured (*meso*) = 234.103

Solution Phase Thermolysis of *meso* and *d,l*-1-(2-Difluoromethylidenecyclopentyl)-2-difluoromethylidenecyclopentane (***meso*-131**,***d,l*-131**)

A 0.160 g sample of 1-(2-Difluoromethylidenecyclopentyl)-2-difluoromethylidenecyclopentane (**131**) was obtained 97% pure by preparative GLPC, being 97% **131** and 3% 1-(2-(1-cyclopentenyl)-1,1,2,2-tetrafluoroethyl)-cyclopentene (**144**). (Column: 0.25 inch x 5.5 feet, 20% QF-1 on Chromosorb WHP 80/100; Oven: constant at 100°C; Injector: 105°C; TCD block: 78°C; He flow: 190 ml/minute; Retention Times: **131** 12.6 minutes, **144** 15.7 minutes)

This material was dissolved in 1.47 g dry, freeze-thaw degassed *n*-dodecane (99+% pure, Aldrich Chemical Co.) and 0.033 g C_6H_5F was added as ^{19}F NMR internal standard. As samples were needed, 0.25 ml aliquots were drawn by syringe and placed in thick walled NMR tubes (base rinsed, deionized water rinsed, acetone rinsed, flame dried) and flame sealed under N_2. Lower temperature rearrangement of ***d,l*-131** to **144** was carried out by thermolyzing the sample for a specific time in a Statim thermostated oil bath then rapidly cooling and storing the sample on ice until ^{19}F NMR analysis. Higher temperature rearrangement of ***meso*-131** to **144** was carried out by thermolyzing the sample for a specific time in the thermostated, gas kinetics apparatus, molten salt bath, then rapidly cooling and storing the sample at room temperature until ^{19}F NMR analysis. The relative concentrations of all reaction components was monitored by integration of the ^{19}F NMR sample signals *versus* internal standard C_6H_5F. A T_1 delay of 10 seconds was applied and a minimum of 128 transients was collected before Fourier transforming and integration of a spectrum. Each sealed sample yielded one rate constant for each diasteromeric component; one from following the rearrangement of ***d,l*-131** at a lower temperature and one from following the rearrangement of ***meso*-131** at an elevated temperature. After collecting sufficient data from a sample for thermolysis of ***d,l*-131** at a given temperature, the sample was then further thermolyzed at the lower temperature until no ***d,l*-131** remained before beginning thermolysis and data collection for ***meso*-131** at elevated temperatures. Rearrangement of ***d,l*-131** was found to follow first-order kinetics and also found to be quantitative and nonreversible towards formation of **144** over the temperature range of 94.0 to 124.1°C. In thermolysis of ***meso*-131**, small amounts of other materials were evidenced by ^{19}F NMR. At longer times in the thermolysis trials, there appeared trace amounts of a series of signals

from -122.6 through -128.7, a total of ten sets of multiplets. The largest couplings observed were on the order of 15 Hz. Also observed at longer times was a singlet of larger intensity at -148.0. Both materials would account for less than 10% of the reaction mixture. The product **144** was obtained for characterization by thermolyzing a crude (90% **131**, 8% THF/diethyl ether, and 2% hexamethylphosphoric triamide) sample of **131** at 140°C for 2 hours then isolating the product away from the unreacted ***meso*-131** by preparative GLPC. (Column: 0.25 inch x 5.5 feet, 20% QF-1 on Chromosorb WHP 80/100; Oven: constant at 130°C; Injector: 140°C; TCD block: 150°C; He flow: 190 ml/minute)

1-(2-(1-Cyclopentenyl)-1,1,2,2-tetrafluoroethyl)cyclopentene (**144**): ^{1}H NMR (300 MHz, $CDCl_3$, TMS) 1.96 (p, 4H, $^{3}J_{HH}$ = 7.54 Hz), 2.40-2.57 (m, 8H), 6.19 (bs, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) 23.3, 31.4 (m, 2C, $^{3}J_{CF}$ = 1.9 Hz), 32.7, 135.9 (m, 2C, $^{3}J_{CF}$ = 4.1 Hz); ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$) -110.5 (s, 4H); Low Resolution Mass Spectrum: m/z (relative intensity): 234 (38), 118 (7), 117 (100), 116 (11), 115 (5), 97 (18), 77 (6), 67 (5); High Resolution Mass Spectrum: Calculated for $C_{12}H_{14}F_4$ = 234.103, Measured = 234.102.

Table 4-15. ^{19}F NMR Ratios for Thermolysis of *d,l* and *meso*-1-(2-Difluoromethylidenecyclopentyl)-2-difluoromethylidenecyclopentane (***d,l*-131**, ***meso*-131**) at 94.0 and 293.1°C.

Thermolysis at 94.0°C

Seconds	%***d,l*-131**	%***meso*-131**	%**144**
0	82.2	15.2	2.6
2220	73.3	15.2	11.5
5940	61.3	15.2	23.5
12660	42.2	15.2	42.6
19080	29.9	15.2	54.9

Table 4-15 - Continued-

-Temperature was then raised to 293.1°C-

Seconds	%*d,l*-131	%*meso*-131	%144
0	0	15.2	84.8
2160	0	13.3	86.7
4260	0	11.9	88.1
7860	0	10.2	89.8

Table 4-16. ^{19}F NMR Ratios for Thermolysis of *d,l*-1-(2-Difluoromethylidenecyclopentyl)-2-difluoromethylidenecyclopentane (***d,l*-131**) at 104.6°C.

Seconds	%*d,l*-131	%*meso*-131	%144
0	81.6	15.7	2.7
1200	70.2	15.7	14.1
2700	57.9	15.7	26.4
4800	44.5	15.7	39.8
7320	32.3	15.7	52.0
13440	14.0	15.7	70.3

Table 4-17. ^{19}F NMR Ratios for Thermolysis of *d,l* and *meso*-1-(2-Difluoromethylidenecyclopentyl)-2-difluoromethylidenecyclopentane (***d,l*-131**, ***meso*-131**) at 117.4 and 274.4°C.

Thermolysis at 117.4°C

Seconds	%***d,l*-131**	%***meso*-131**	%144
0	81.9	15.4	2.7
900	60.3	15.4	24.3
2760	30.0	15.4	54.6
4020	19.6	15.4	65
6120	8.9	15.4	75.7

Temperature was then raised to 274.4°C

Seconds	%***d,l*-131**	%***meso*-131**	%144
0	0	15.4	84.6
2700	0	14.4	85.6
6900	0	13.8	86.2
15660	0	12.5	87.5
27480	0	10.7	89.3
43560	0	9.3	90.7

Table 4-18. ^{19}F NMR Ratios for Thermolysis of *d,l* and *meso*-1-(2-Difluoromethylidenecyclopentyl)-2-difluoromethylidenecyclopentane (***d,l*-131**, ***meso*-131**) at 124.0 and 288.1°C

Thermolysis at 124.0°C

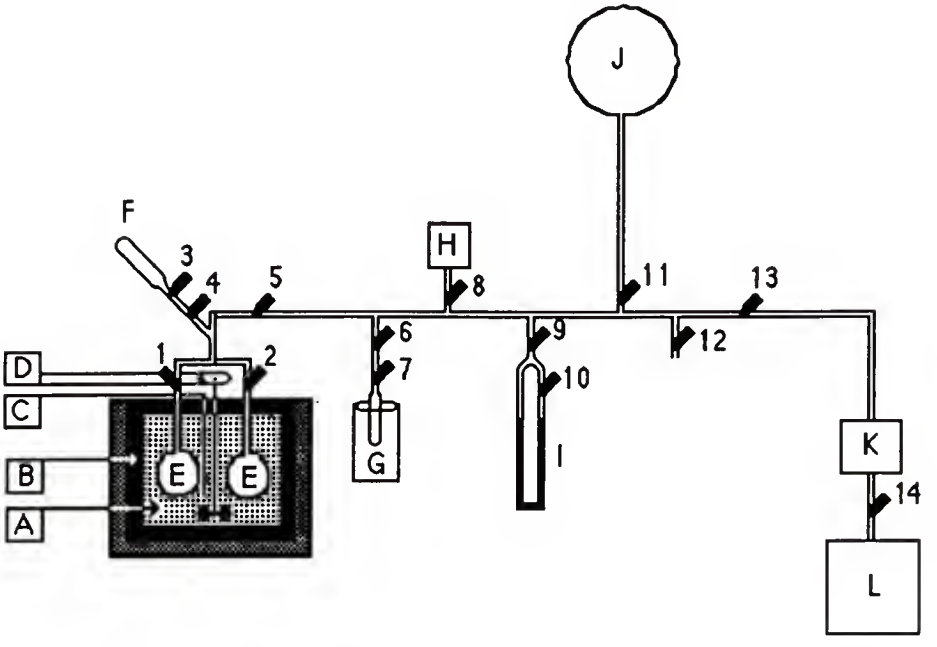
Seconds	%***d,l*-131**	%***meso*-131**	%**144**
0	80.4	15.3	4.3
540	61.1	15.3	23.6
1140	44.5	15.3	40.2
2340	22.0	15.3	62.7
4260	6.9	15.3	77.8

Temperature was then raised to 288.1°C

Seconds	%***d,l*-131**	%***meso*-131**	%**144**
0	0	15.3	84.7
1680	0	14.2	85.8
3900	0	12.9	87.1
11100	0	10.3	89.7
15540	0	8.8	91.2

APPENDIX A

GAS PHASE THERMOLYSIS APPARATUS



Key. 1-14 Rotaflow joints, A: molten salt bath, 1:1 by weight of $NaNO_2$, KNO_3, B:resistance coil, C: thermocouples, D: stirrer, E: 250 ml Pyrex kinetic bulbs, F: Rotaflow sampling tube, G: starting material stock in Rotaflow tube, H: Pirani PR10-C gauge head, I: Hg U-tube manometer, J: 5 L ballast at ≈ 760 mm Hg of argon, K: liquid nitrogen trap, L: vacuum pump

Figure A-1. Diagram of Gas Kinetics Apparatus.

All thermal isomerizations were carried out in conditioned, spherical Pyrex 250 ml bulbs. These bulbs were submerged in a stirred (D) molten salt bath (A, eutectic mixture, 1:1 by weight of $NaNO_2$, KNO_3, mp ≈ 180°C). The bath was heated by a resistance coil (B) and temperature set and maintained by an Omega Model 49 Proportioning Controller with platinum resistance thermocouple. The temperature for a run was measured with an Omega Model

HH22 Microprocessor Thermometer with a type J (Fe-CuNi) thermocouple. The thermocouples were immersed in the salt bath directly between the pyrolysis vessels (C). The temperatures were found to be constant to within 0.1°C over a run.

A typical run involves the following general procedure. The line and pyrolysis vessels are pumped down with a high capacity, Welch Duo-Seal rotary vane vacuum pump (L) and the ultimate vacuum (≈ 10^{-3} mm Hg) monitored with an Edwards Pirani Model 11 display and Pirani model PR10-C gauge head (H). The pump and liquid nitrogen trap (K) are sealed off (13) and an initial pressure of 8 ± 0.5 mm Hg of starting material (measured with a Hg U-tube manometer, I) is introduced into the vacuum line by expansion from a cooled Rotaflow tube (G). A sample is then expanded into the kinetics vessels (E, 1 and 2) and timing started for the run. The excess starting material remaining in the line at this time is condensed into the storage vessel (G) and the line is pumped down. At a desired time, the pump is cut out (5) and a sample expanded into the sampling Rotaflow tube (F). The pump is then cut out (13) and the sample dilluted with argon from a five liter bulb (J) to create a sample with a total pressure of approximately 500 - 760 mm Hg, and removed to make multiple GLPC injections *via* a gas sampling valve. The pump is then cut in (5, 13) and the line pumped down with a fresh sampling tube (F) in preparation for the next sample.

Each kinetic thermolysis run was sampled at least five times. A Hewlett Packard 5890 Series II gas chromatograph with a flame ionization detector and a Hewlett Packard 3396A integrator was used to analyze the samples drawn. Base-line resolution of peaks was observed for all quantitative GLPC studies. Each point in a rate constant is an average of at least three GLPC injections.

The gas sampling technique utilized in all of the above-described studies introduced multiple pressure variations *per* run. The fact that good unimolecular behavior was always observed indicates clearly the lack of significant surface effect problems. The kinetic apparatus is modeled after the apparatus and technique of Dr. H. M. Frey, University of Reading, England.

APPENDIX B

SELECTED ^{19}F NMR SPECTRA

The ^{19}F NMR spectra of new compounds are graphically illustrated in this appendix. The spectra are presented numerically in their respective areas in Chapter 4. The compounds ***E*-56** and ***Z*-56** have been previously reported as discussed in Chapter 2. The spectra are shown in order of their dissertation identification number and the compounds which have been included in this appendix are: **40** (at -17.0°, 25.0°C, and 80.0°C), **41**, **49**, **50**, **51**, ***E*-56**, ***Z*-56**, **62**, **63**, **123**, **124**, ***meso*-131**, ***d,l*-131**, and **144**.

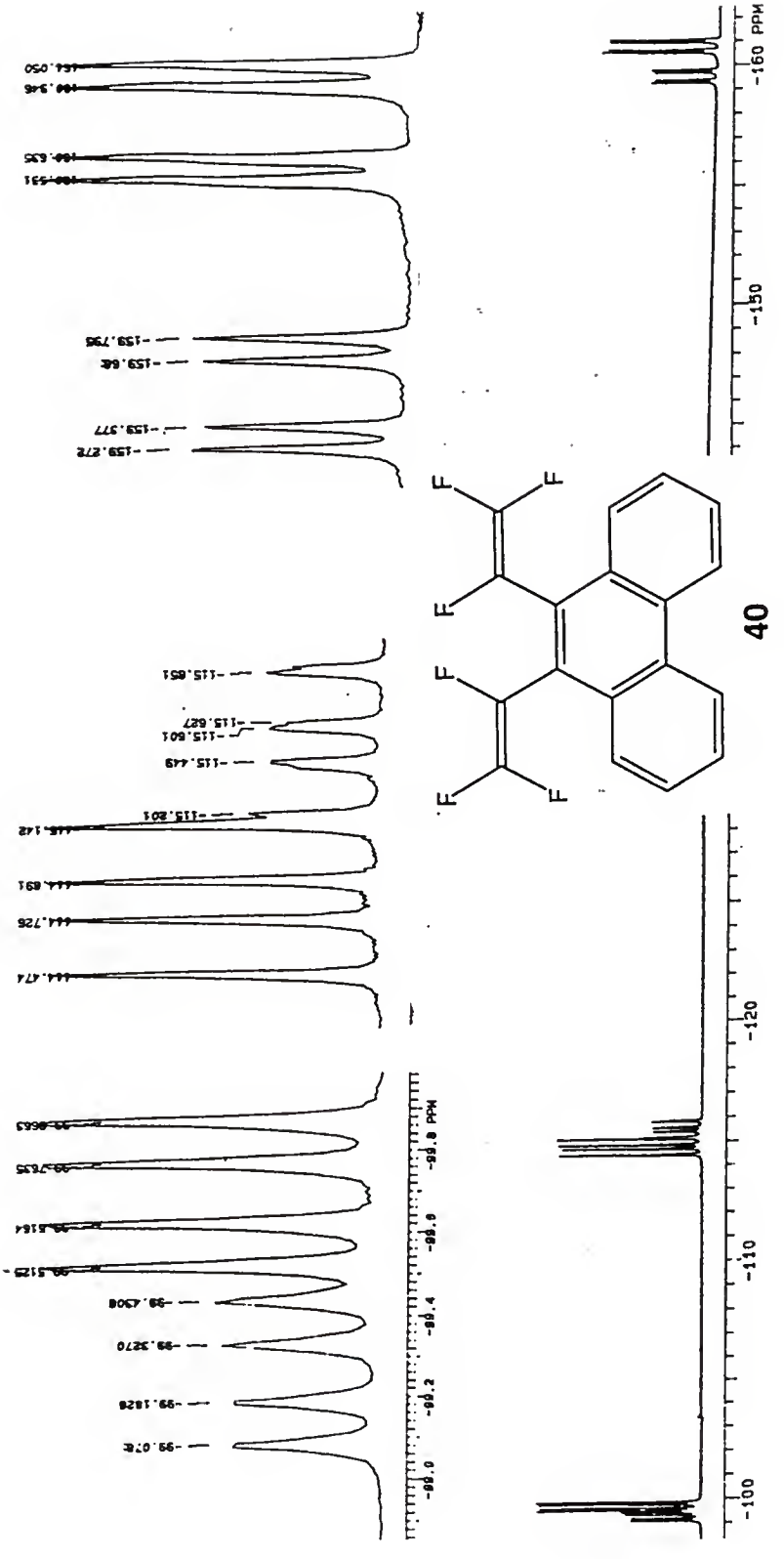


Figure B-1. 9,10-Bis(trifluoroethenyl)phenanthrene (**40**) at -17.0°C in $CDCl_3$.

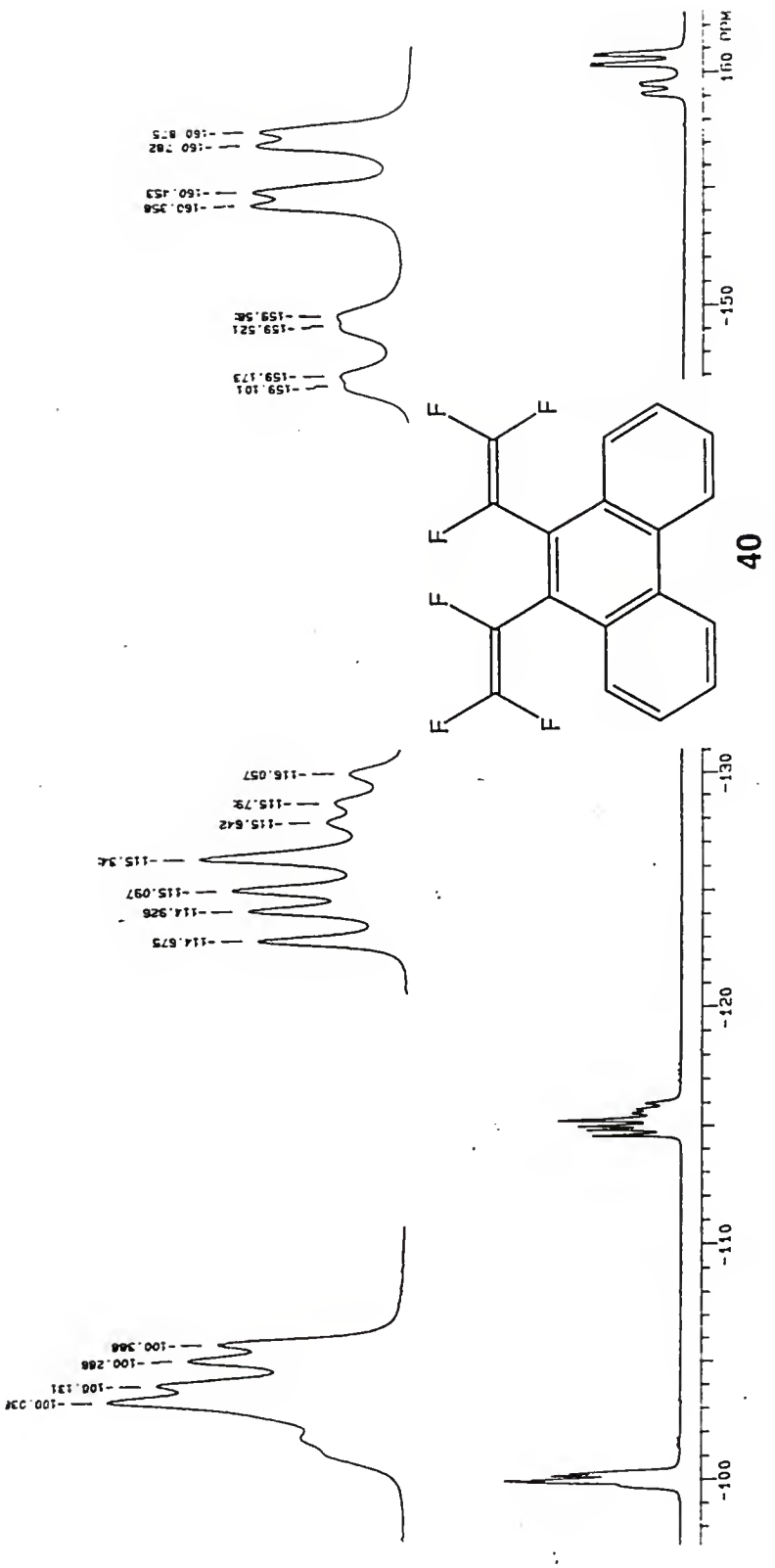


Figure B-2. 9,10-Bis(trifluoroethenyl)phenanthrene (**40**) at 25.0°C in $CDCl_3$.

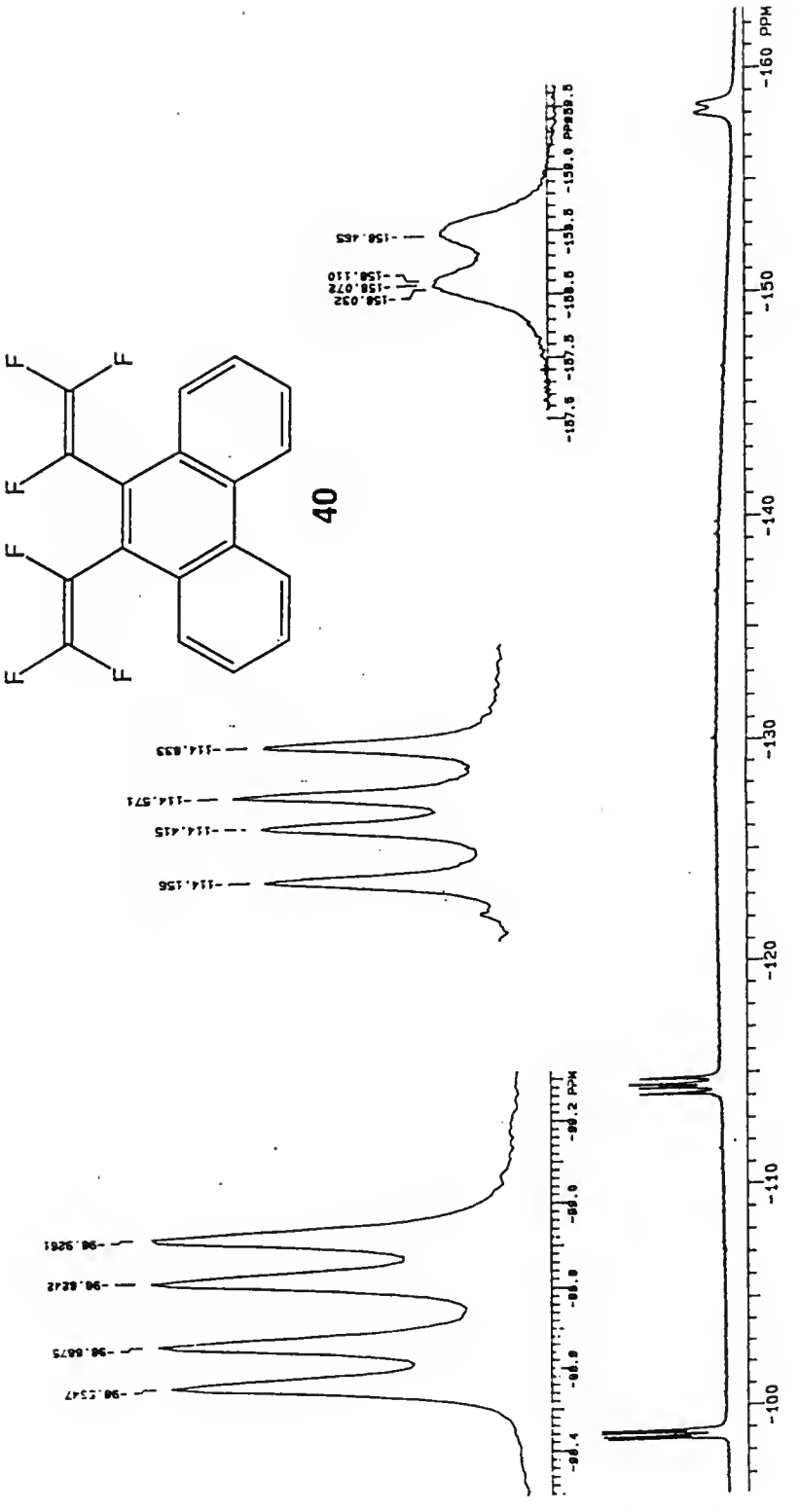
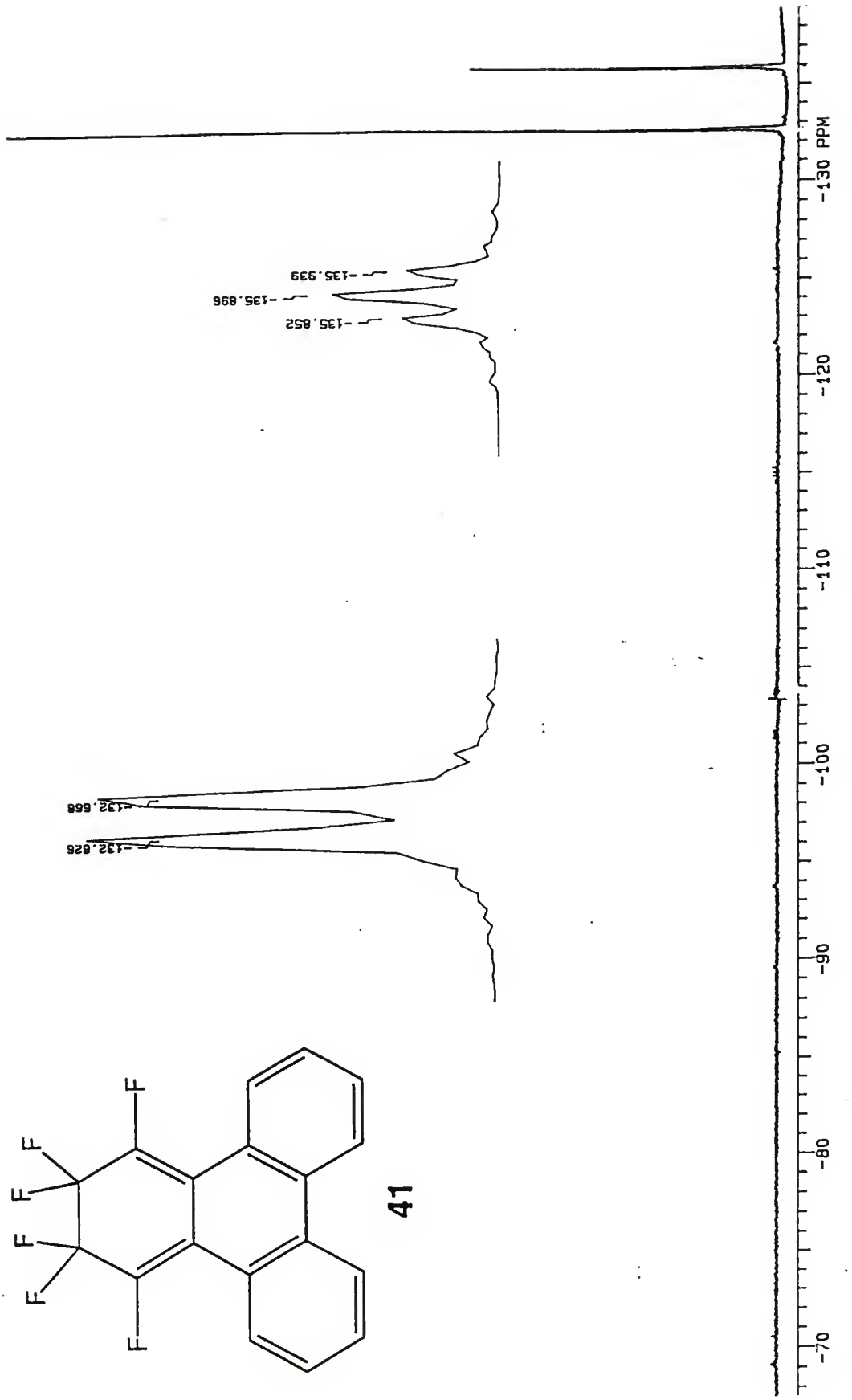
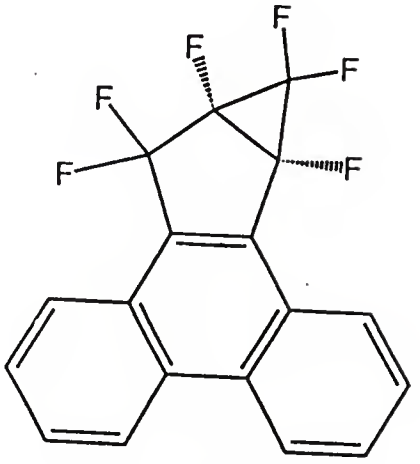


Figure B-3. 9,10-Bis(trifluoroethenyl)phenanthrene (**40**) at 80.0°C in $CDCl_3$.



41

Figure B-4. 1,2,2,3,3,4-Hexafluoro-2,3-dihydrotriphenylene (**41**) in $CDCl_3$.



49

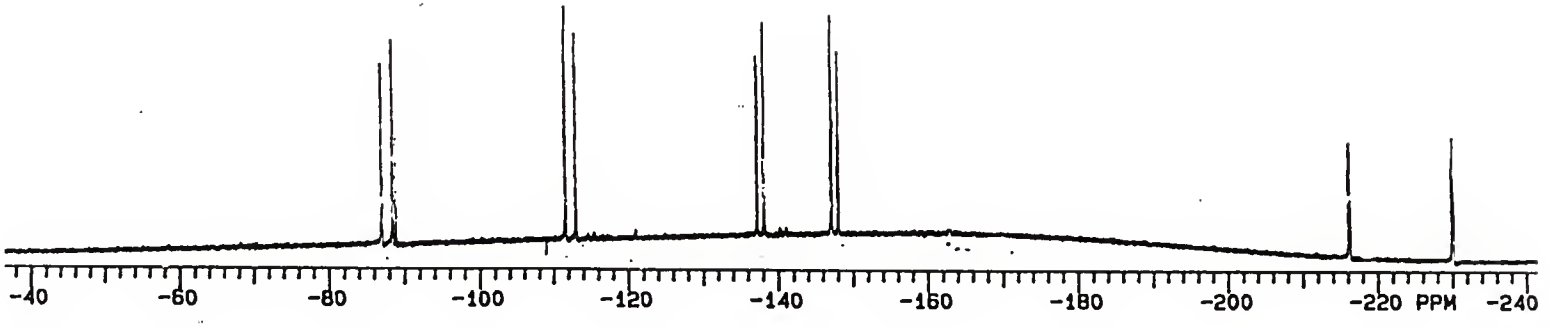


Figure B-5. 1,4,4,5,6,6-Hexafluoro-2,3-(9,10-phenanthro)bicyclo[3.1.0]hex-2-ene (**49**) in $CDCl_3$.

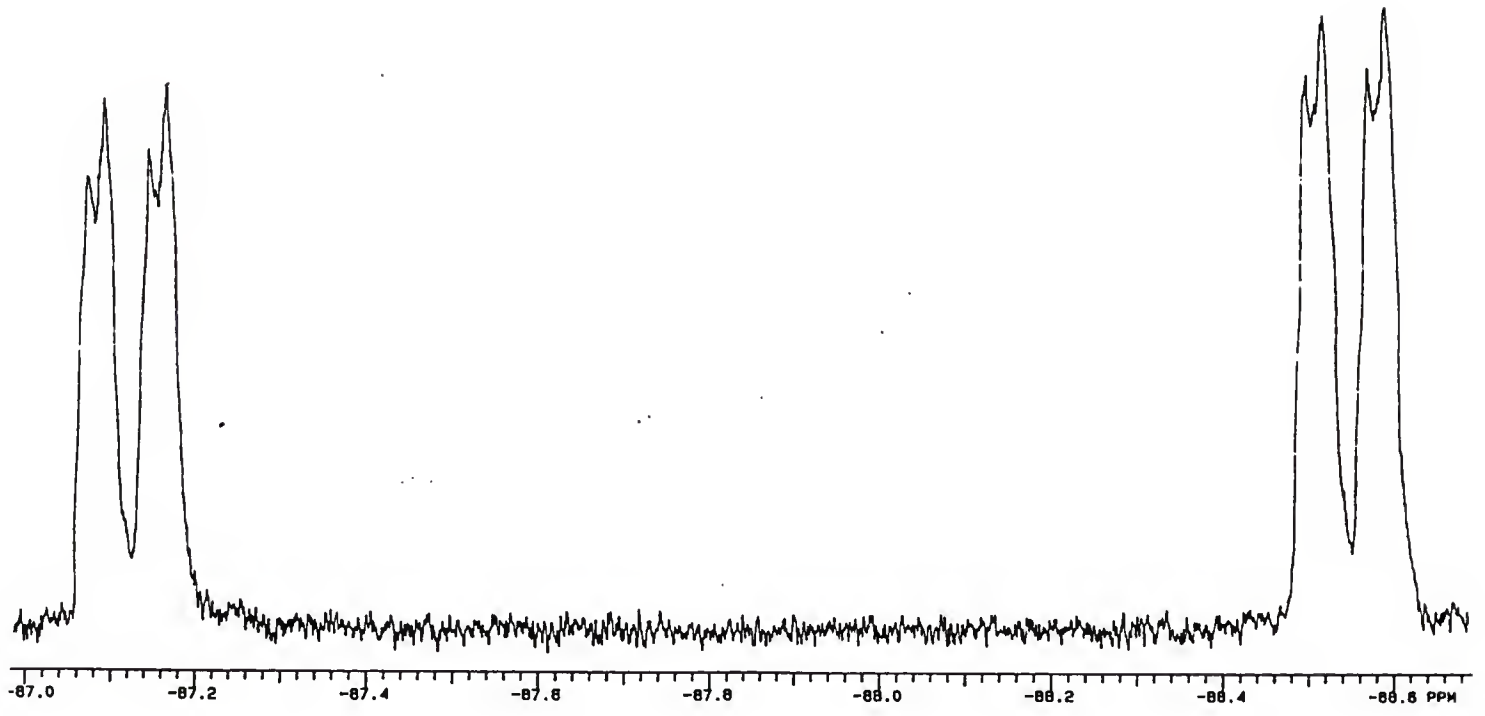


Figure B-6. Expansion 1 of 6 for the 87.0 - 88.6 ppm Region of 1,4,4,5,6,6-Hexafluoro-2,3-(9,10-phenanthro)bicyclo[3.1.0]hex-2-ene (**49**) in $CDCl_3$.

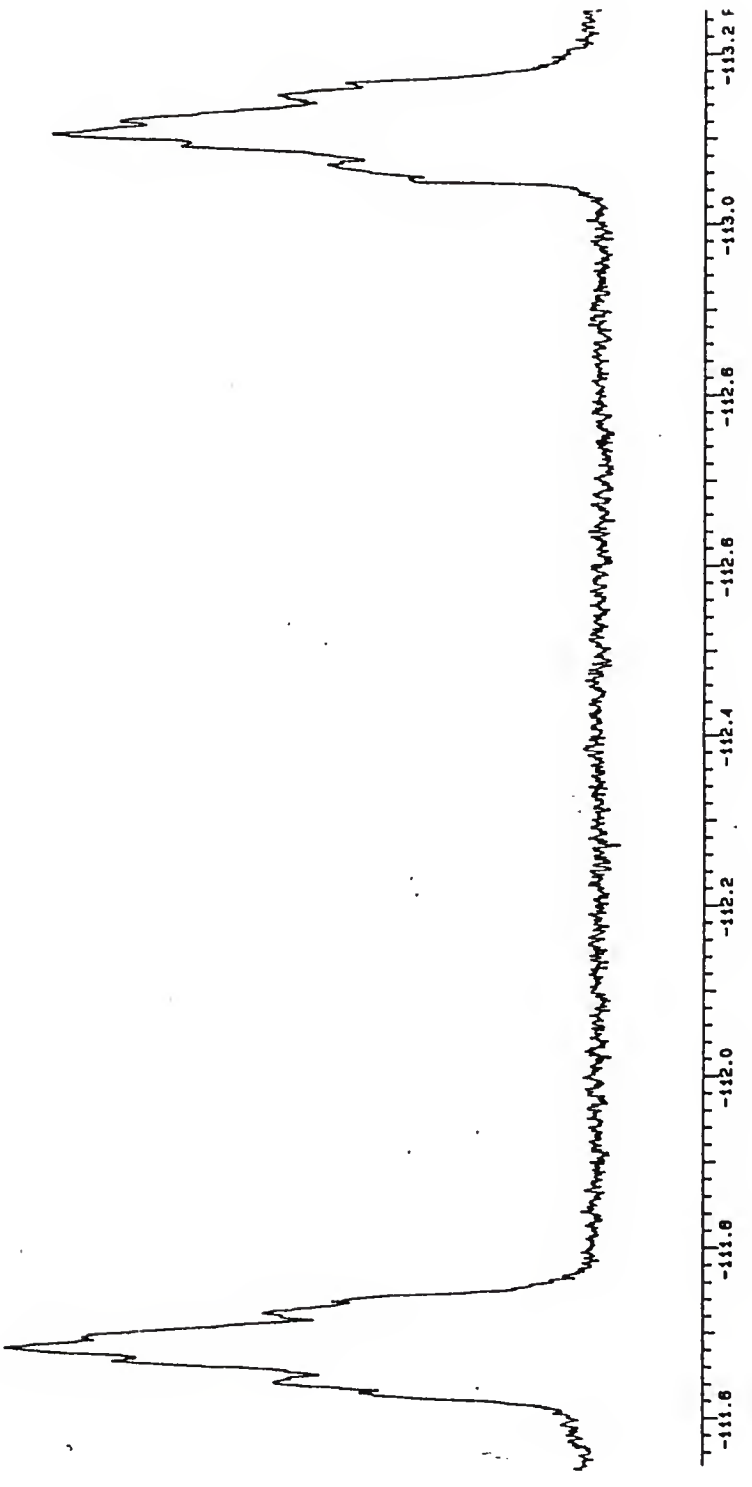


Figure B-7. Expansion 2 of 6 for the 111.6 - 113.3 ppm Region of 1,4,4,5,6,6-Hexafluoro-2,3-(9,10-phenanthro)bicyclo[3.1.0]hex-2-ene (**49**) in $CDCl_3$.

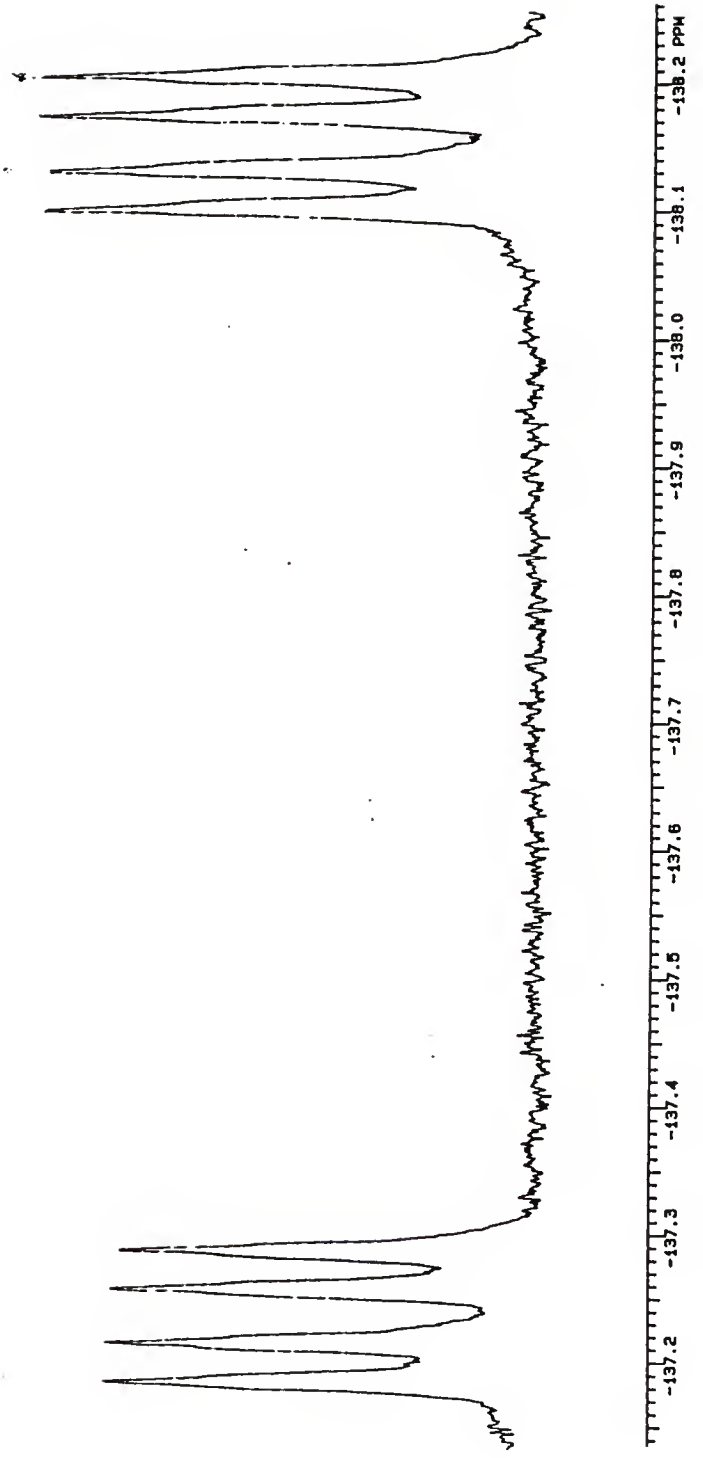


Figure B-8. Expansion 3 of 6 for the 137.1 - 138.3 ppm Region of 1,4,4,5,6,6-Hexafluoro-2,3-(9,10-phenanthro)bicyclo[3.1.0]hex-2-ene (**49**) in $CDCl_3$.

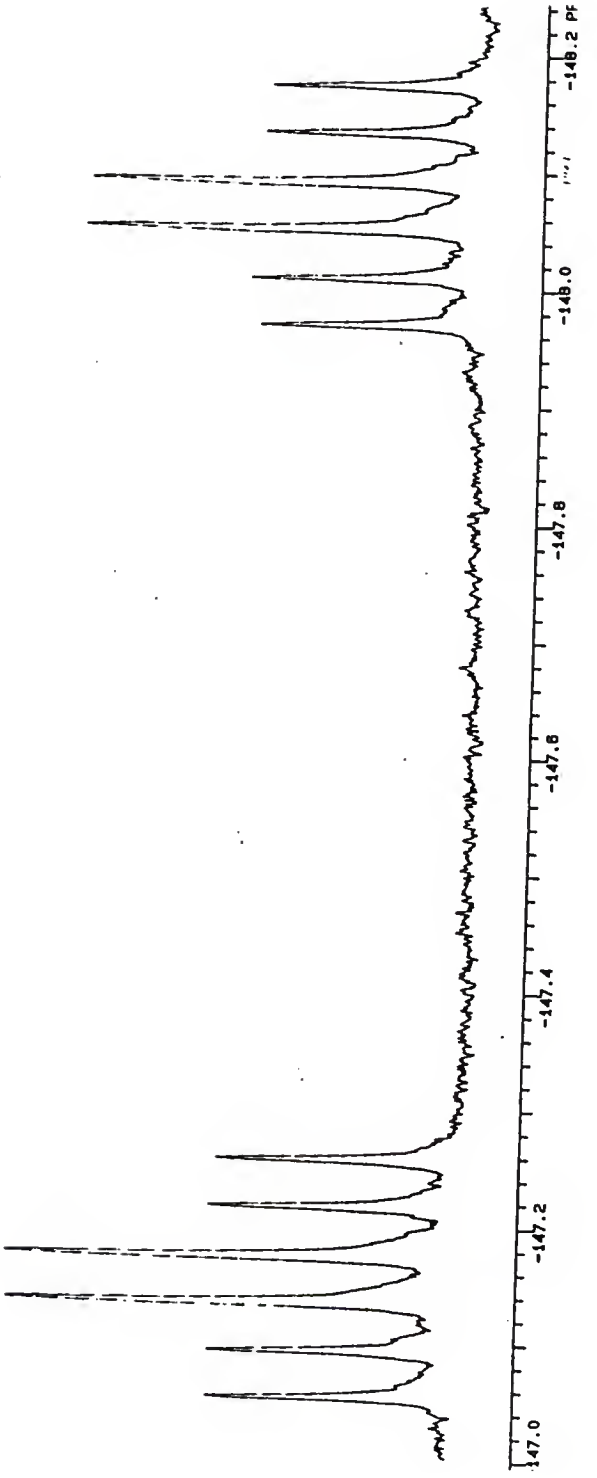


Figure B-9. Expansion 4 of 6 for the 147.0 - 148.2 ppm Region of 1,4,4,5,6,6-Hexafluoro-2,3-(9,10-phenanthro)bicyclo[3.1.0]hex-2-ene (**49**) in $CDCl_3$.

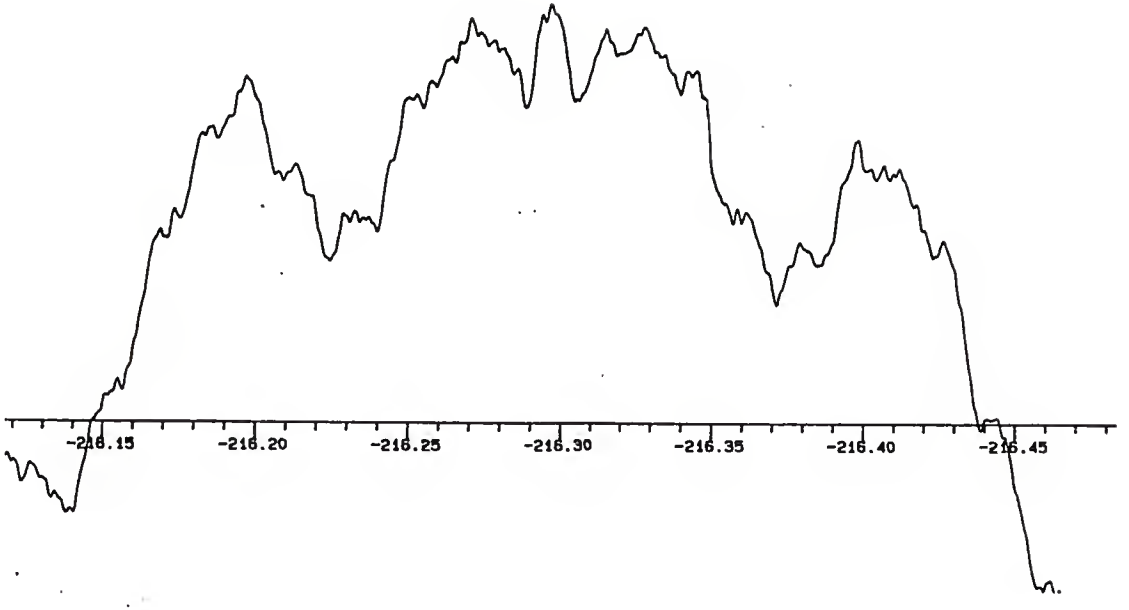


Figure B-10. Expansion 5 of 6 for the 216.15 - 216.45 ppm Region of 1,4,4,5,6,6-Hexafluoro-2,3-(9,10-phenanthro)bicyclo[3.1.0]hex-2-ene (**49**) in $CDCl_3$.

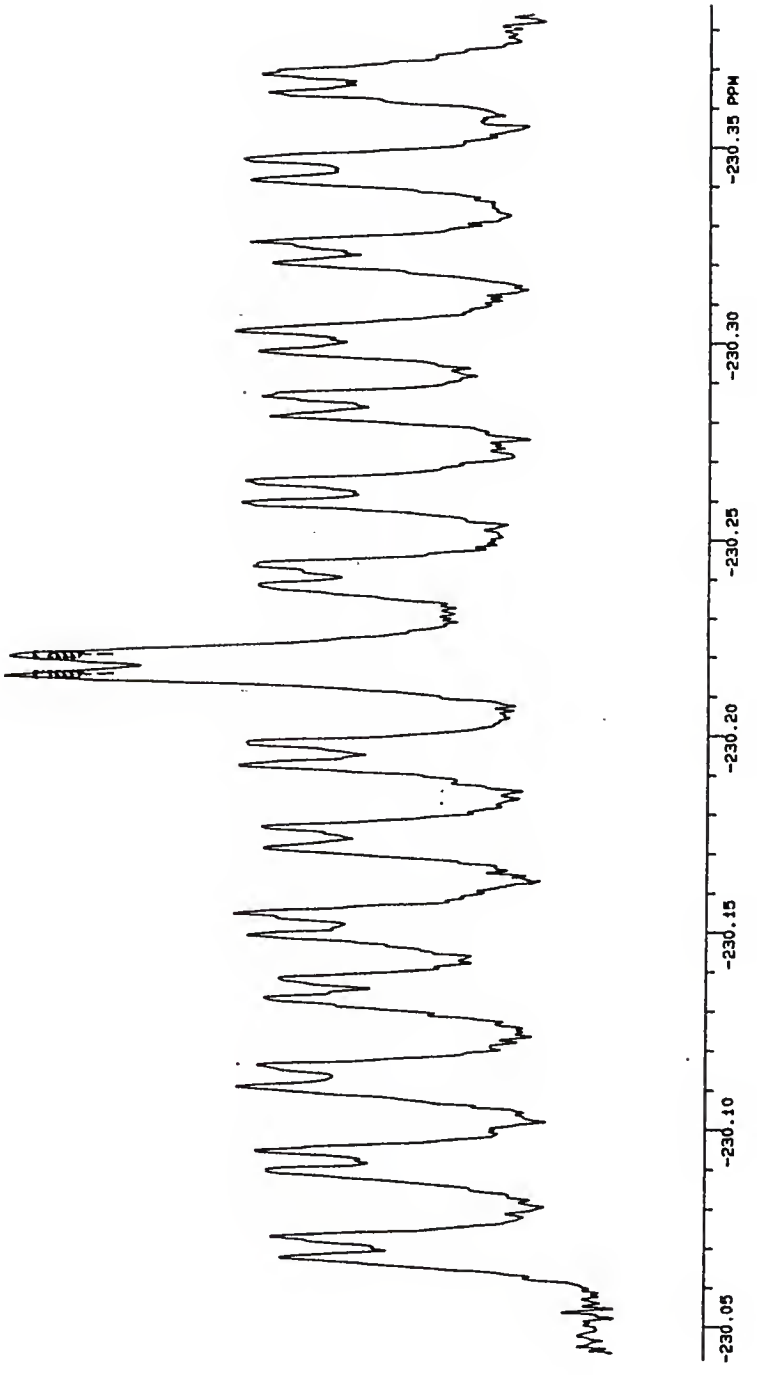


Figure B-11. Expansion 6 of 6 for the 230.05 - 230.38 ppm Region of 1,4,4,5,6,6-Hexafluoro-2,3-(9,10-phenanthro)bicyclo[3.1.0]hex-2-ene (**49**) in $CDCl_3$.

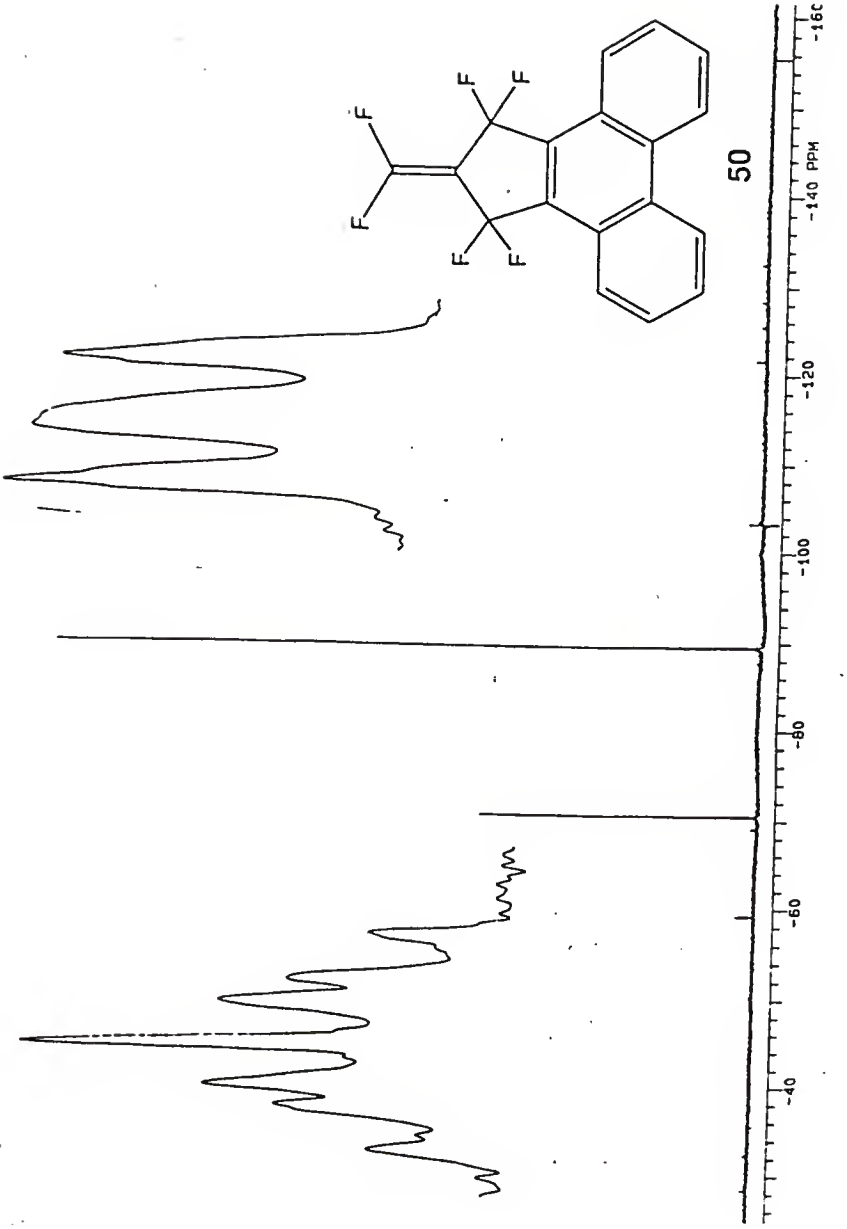


Figure B-12. 4-Difluoromethylidene-3,3,5,5-tetrafluoro-1,2-(9,10-phenanthro)cyclopent-1-ene (**50**) in $CDCl_3$.

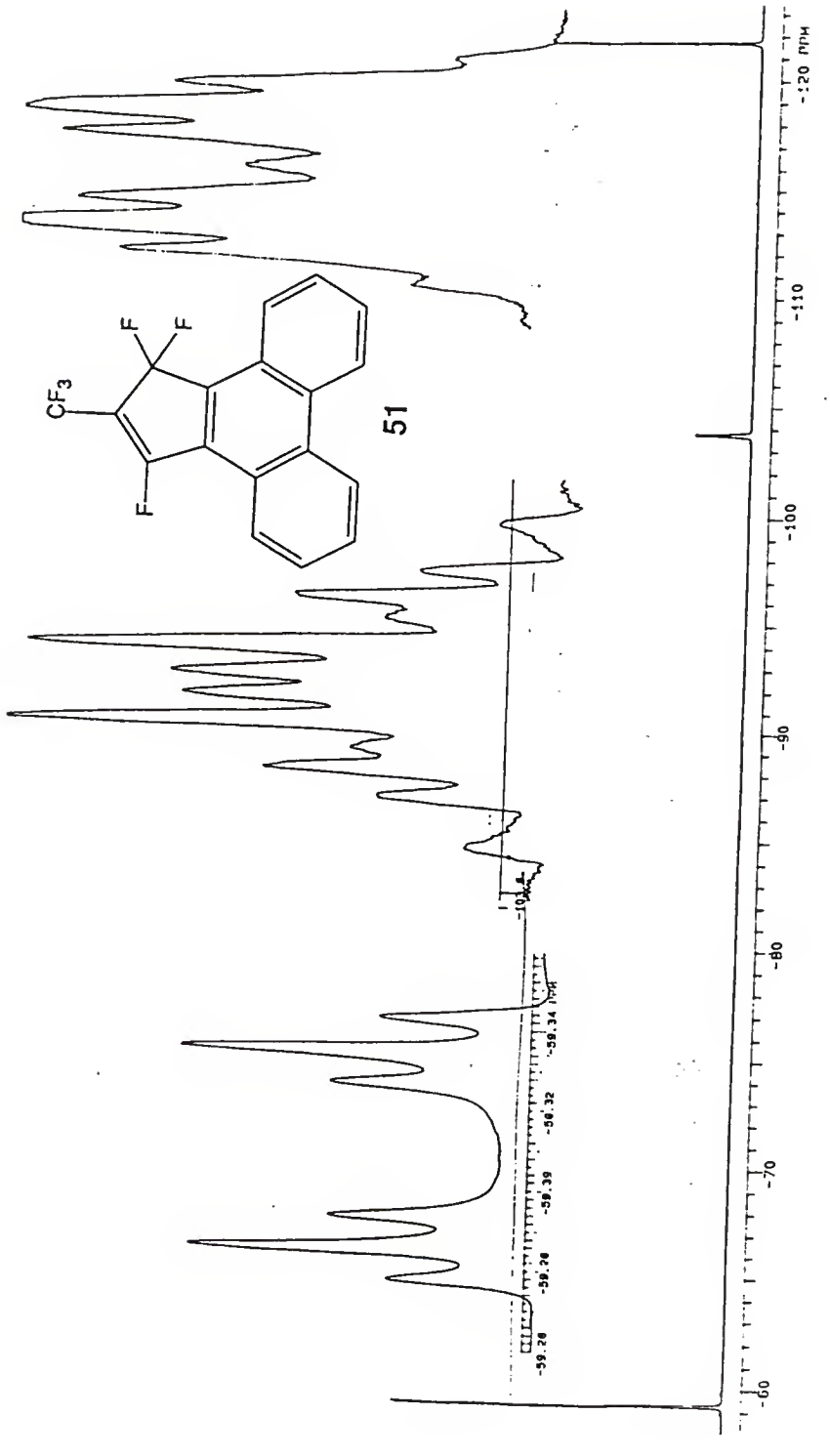


Figure B-13. 1,2-(9,10-Phenanthro)-3,5,5-trifluoro-4-trifluoromethyl-1,3-cyclopentadiene (**51**) in $CDCl_3$.

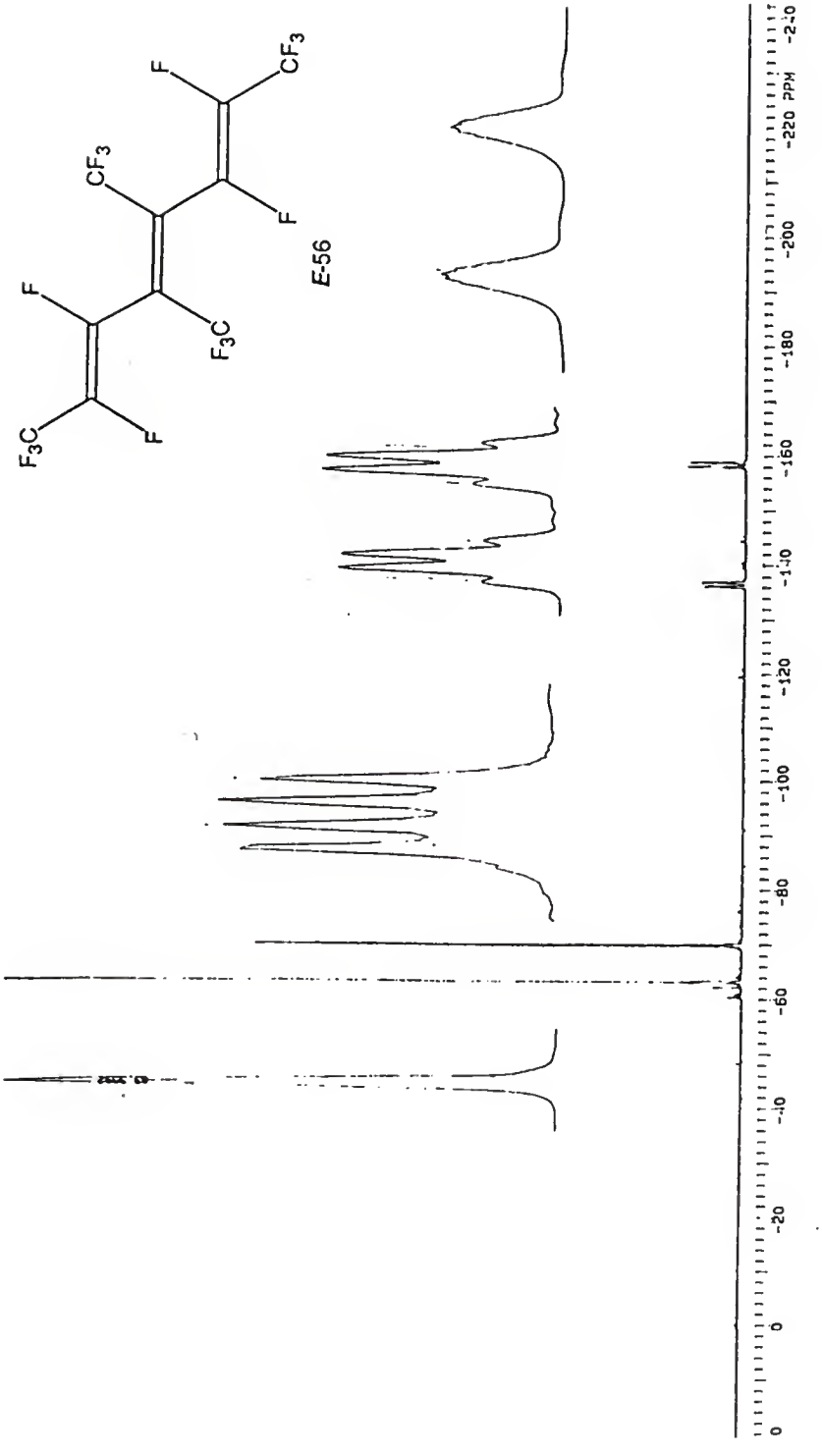


Figure B-14. Perfluoro-*E*,*E*,*E*-4,5-dimethyl-2,4,6-octatriene (***E*-56**) in *n*-Pentane.

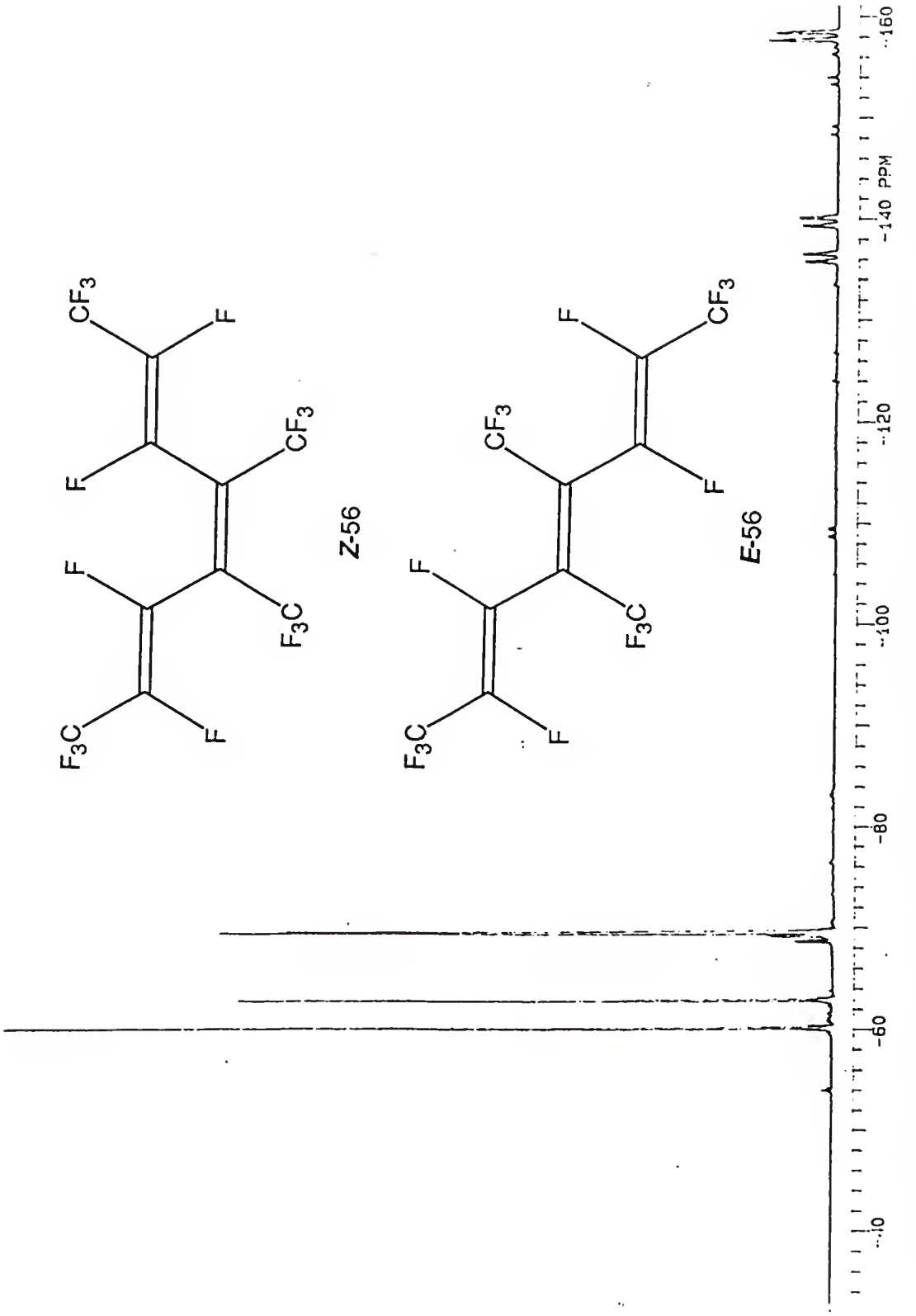


Figure B-15. Perfluoro-*E,Z,E*- and *E,E,E*-4,5-dimethyl-2,4,6-octatriene (**Z-56**(***E*-56**)) in *n*-Pentane.

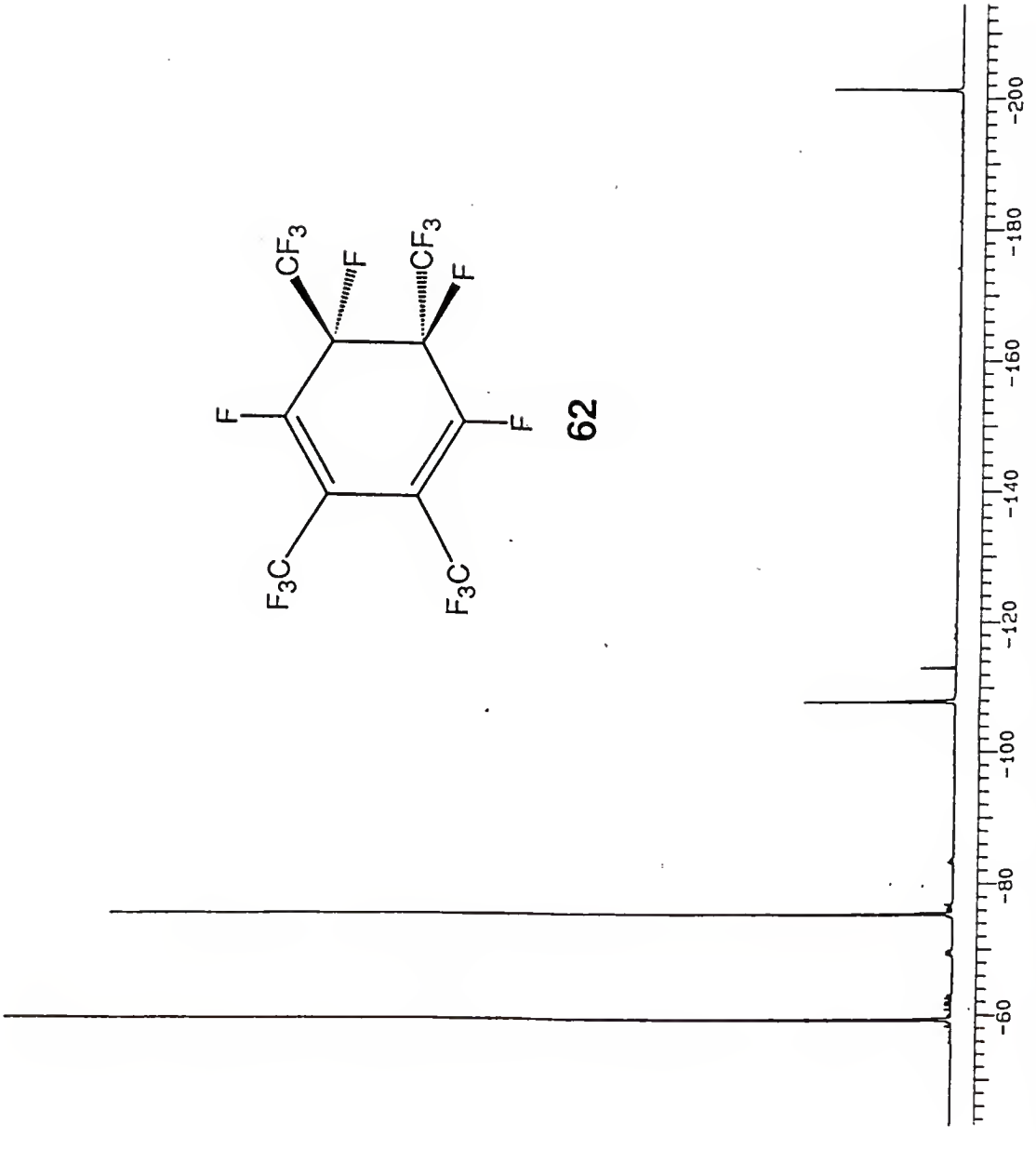


Figure B-16. Perfluoro-*trans*-2,3,5,6-tetramethyl-1,3-cyclohexadiene (**62**) in *n*-Pentane.

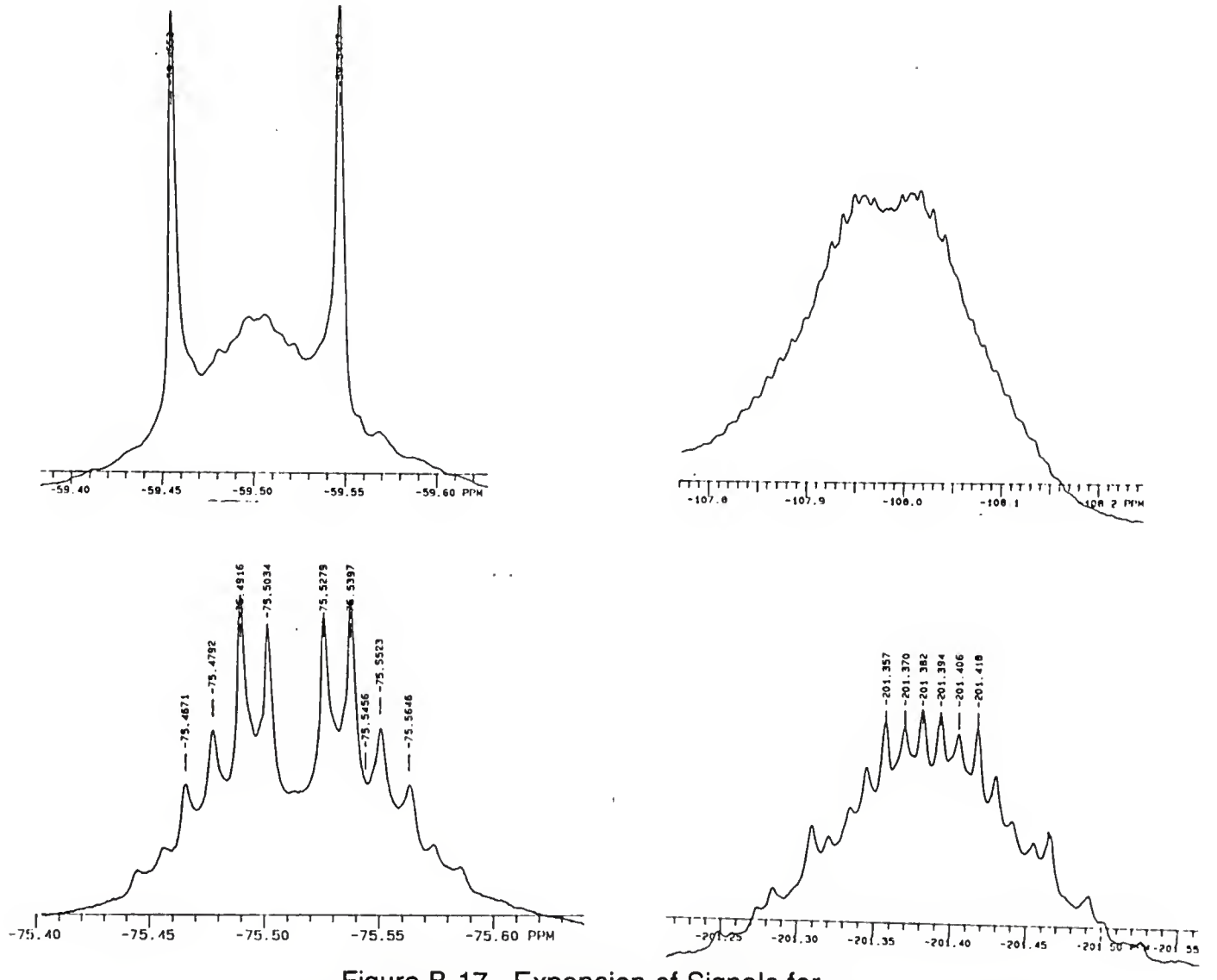


Figure B-17. Expansion of Signals for
Perfluoro-*trans*-2,3,5,6-tetramethyl-1,3-cyclohexadiene (**62**) in *n*-Pentane.

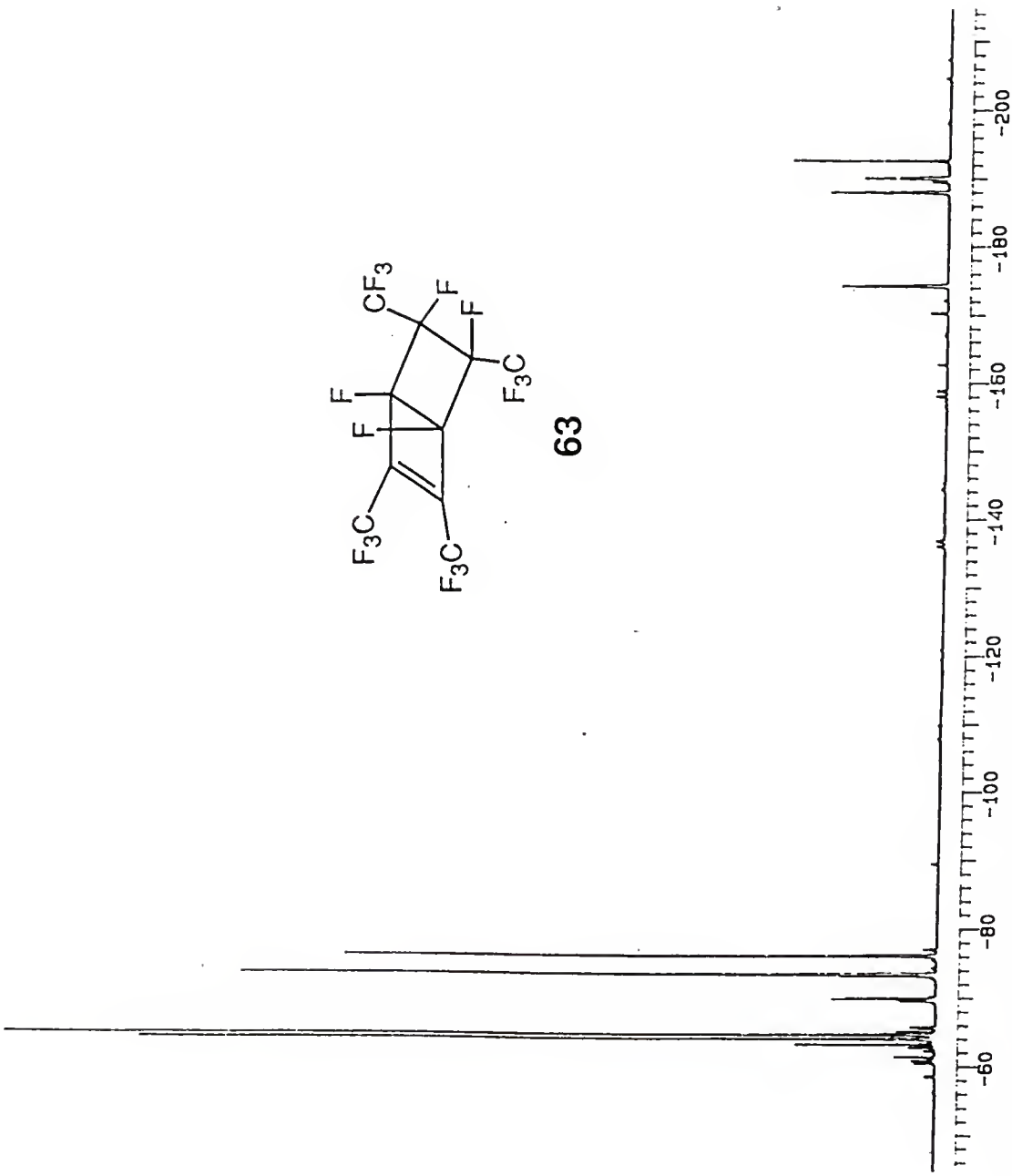


Figure B-18. Perfluoro-*trans*-2,3,5,6-tetramethylbicyclo[2.2.0]hex-2-ene (**63**) in *n*-Pentane.

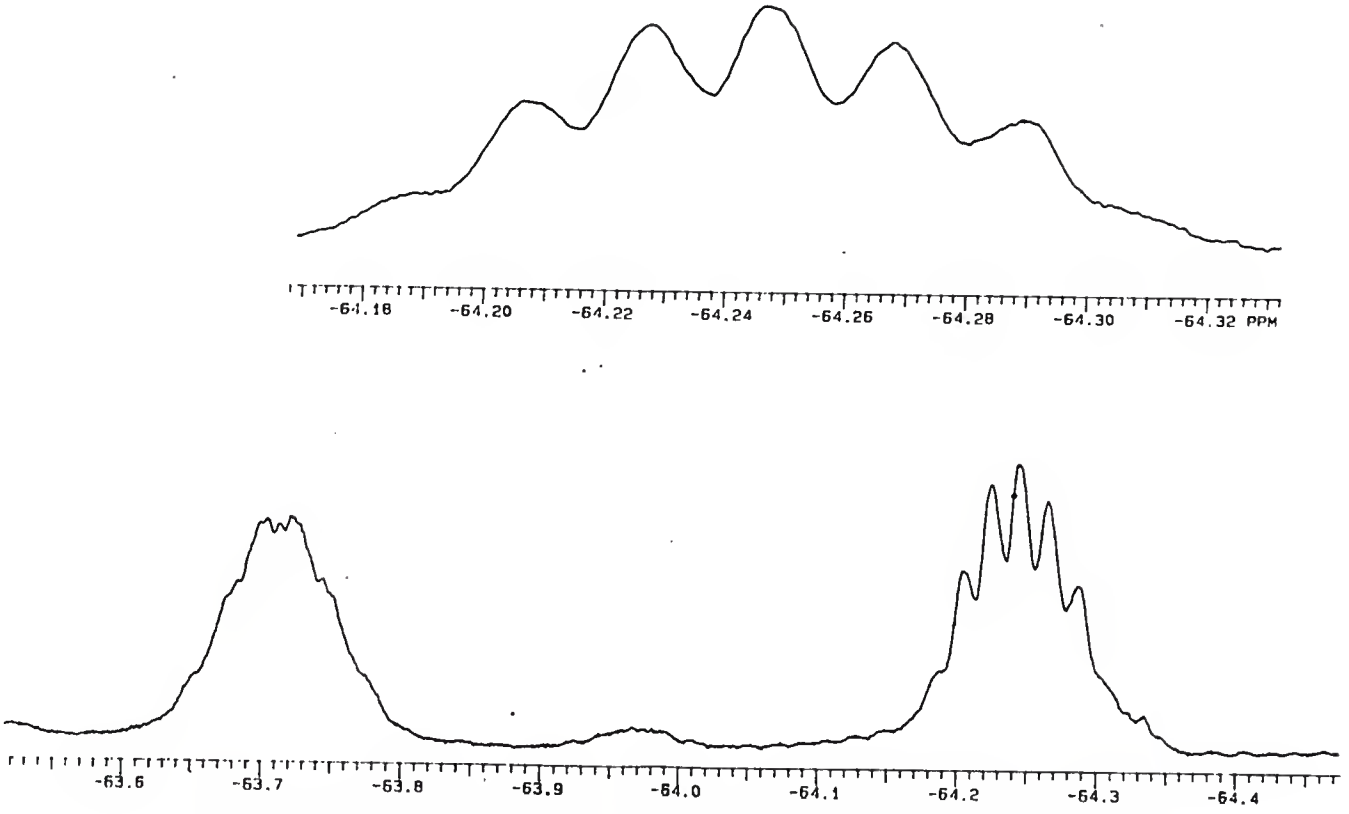


Figure B-19. Expansion 1 of 3 for the 63.6 to 64.4 ppm Region of Perfluoro-*trans*-2,3,5,6-tetramethylbicyclo[2.2.0]hex-2-ene (**63**) in *n*-Pentane.

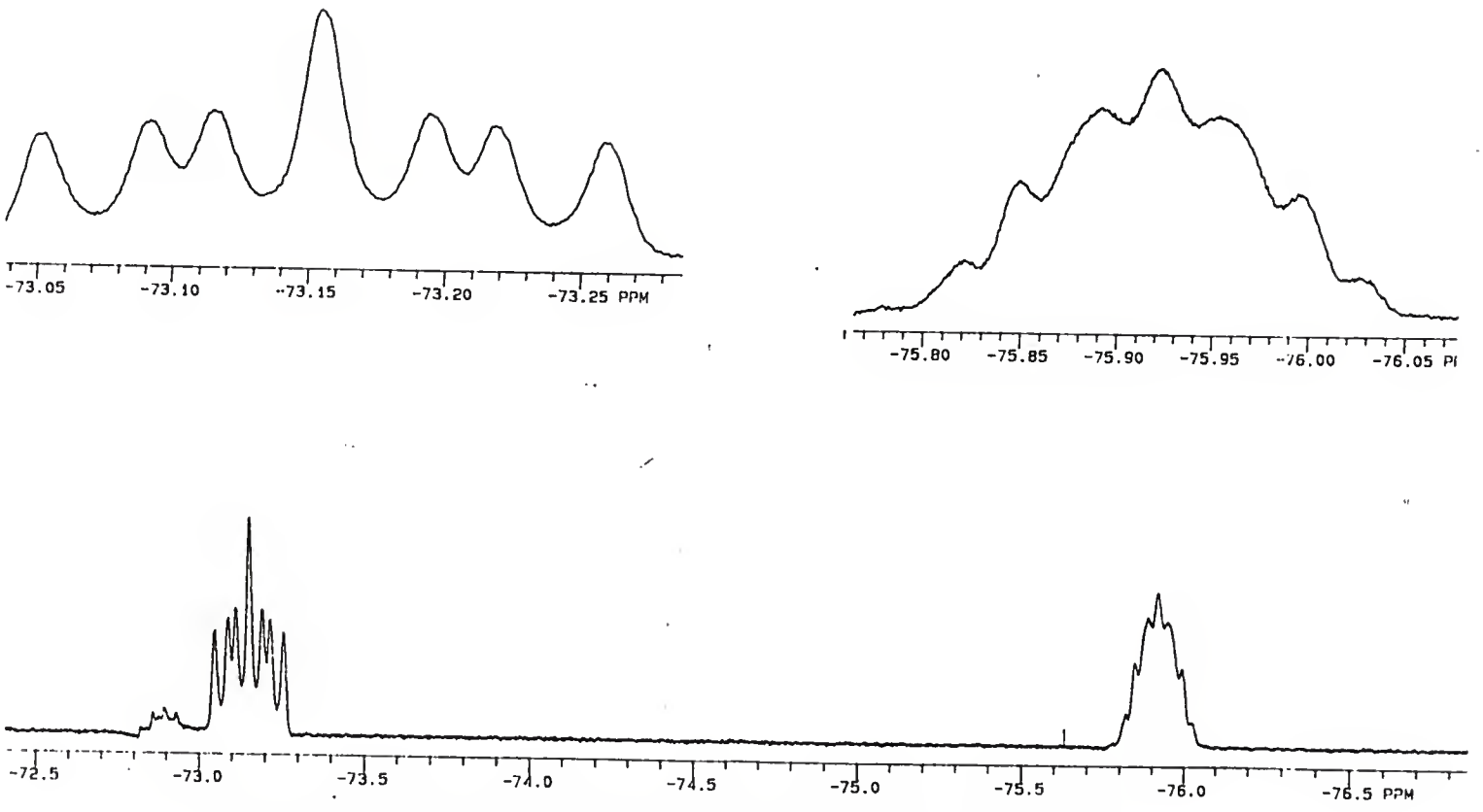


Figure B-20. Expansion 2 of 3 for the 72.5 to 76.5 ppm Region of Perfluoro-*trans*-2,3,5,6-tetramethylbicyclo[2.2.0]hex-2-ene (**63**) in *n*-Pentane.

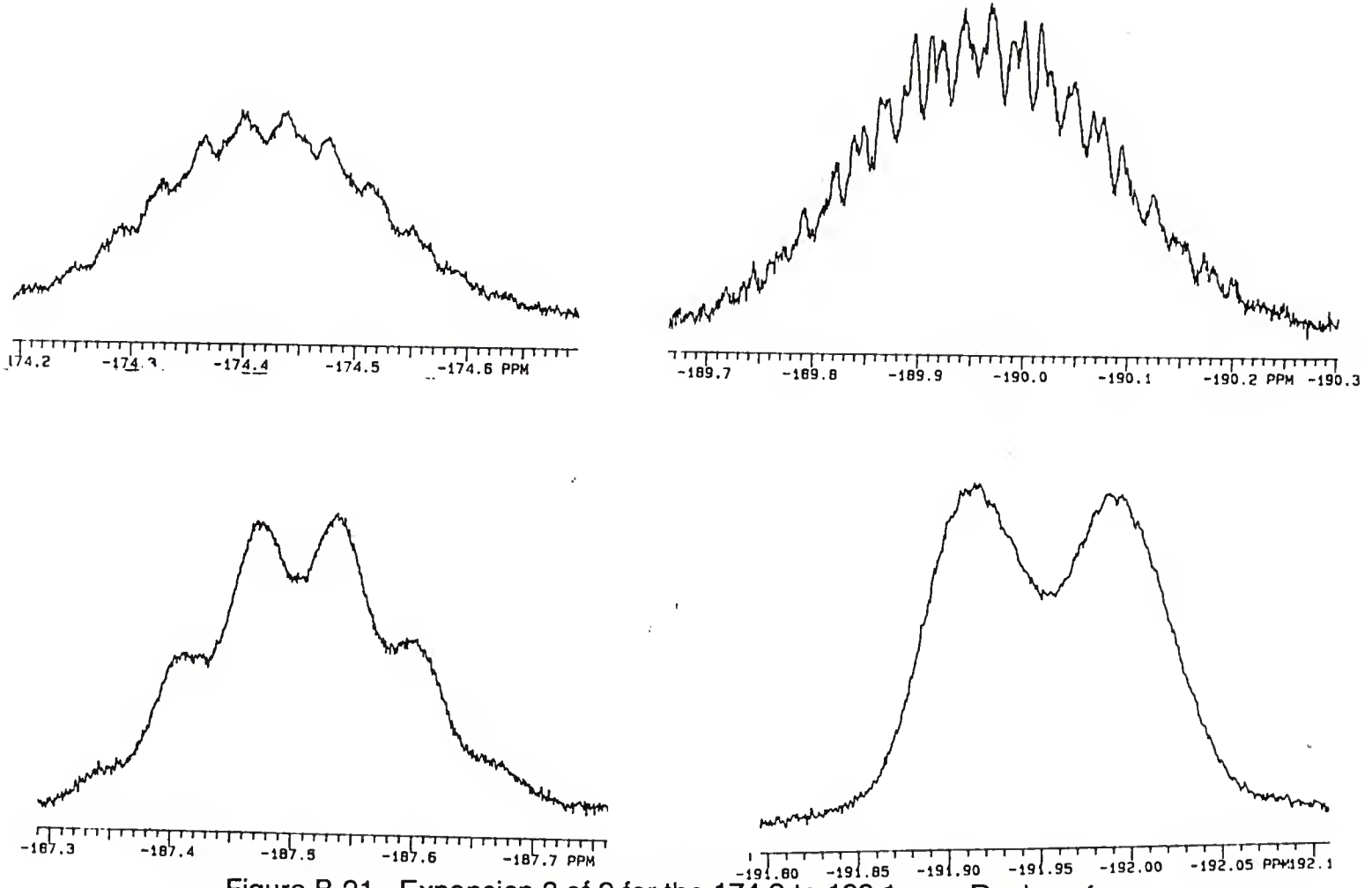


Figure B-21. Expansion 3 of 3 for the 174.2 to 192.1 ppm Region of Perfluoro-*trans*-2,3,5,6-tetramethylbicyclo[2.2.0]hex-2-ene (**63**) in *n*-Pentane.

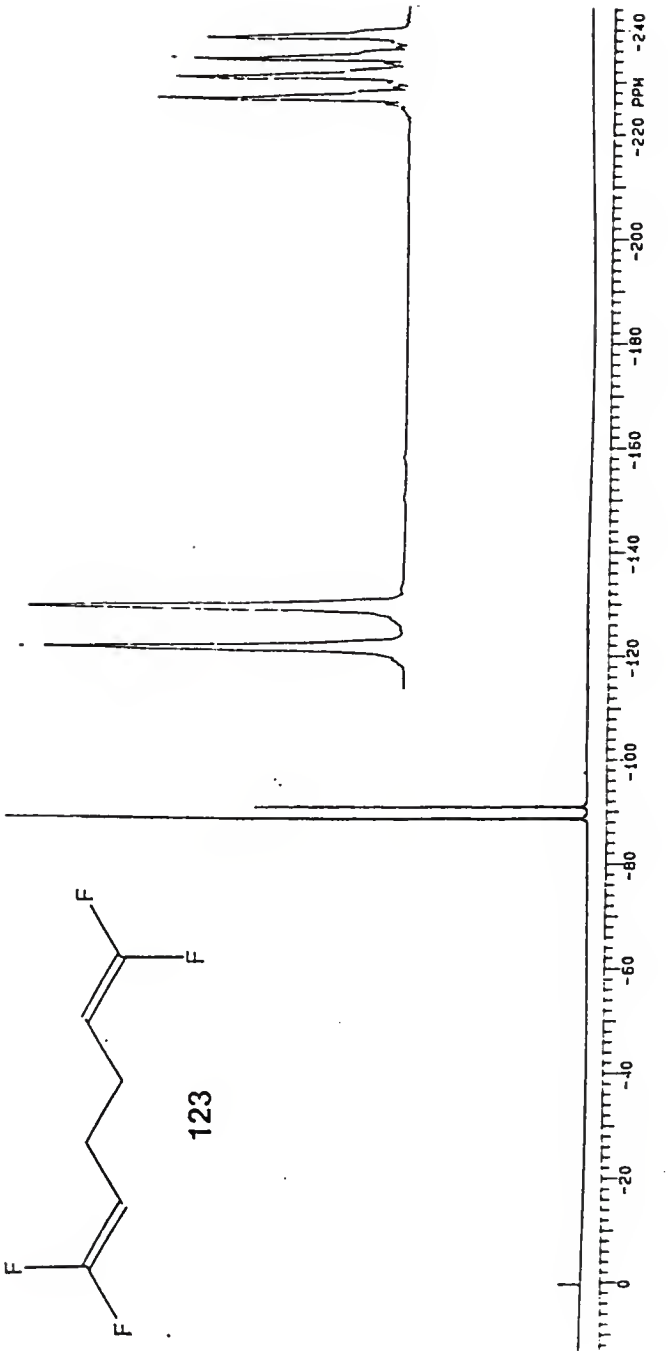


Figure B-22. 1,1,6,6-Tetrafluoro-1,5-hexadiene (**123**) in $CDCl_3$.

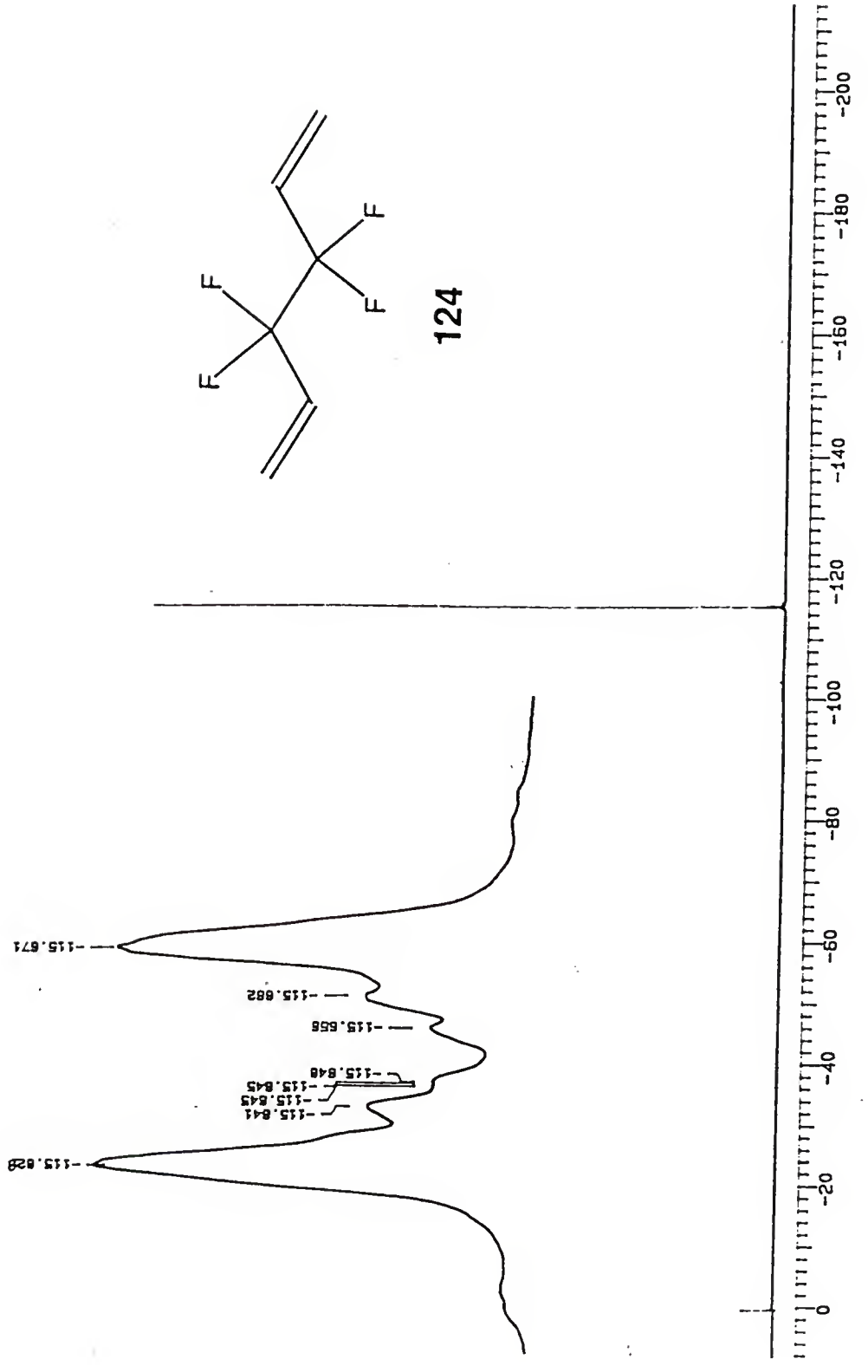


Figure B-23. 3,3,4,4-Tetrafluoro-1,5-hexadiene (**124**) in $CDCl_3$.

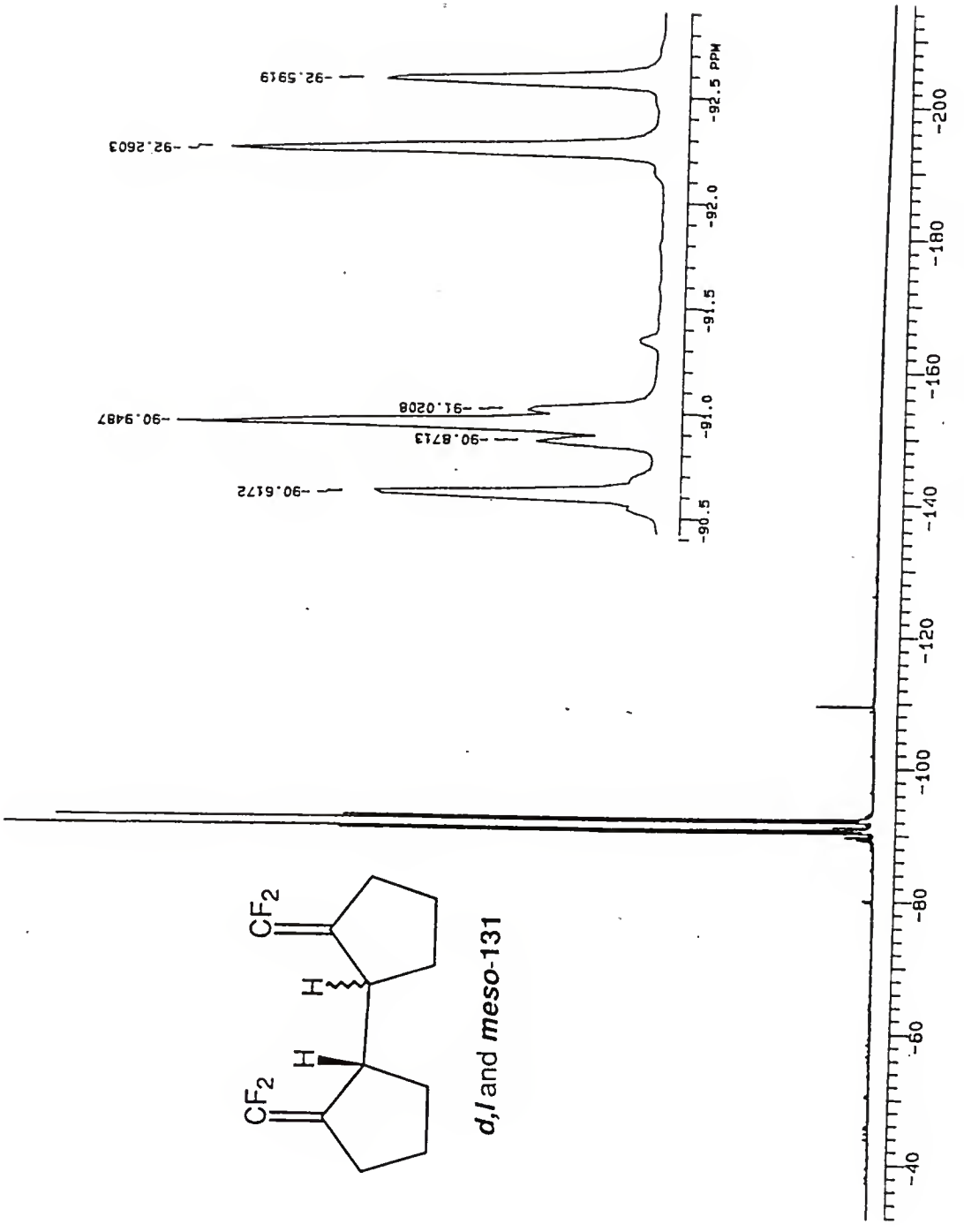


Figure B-24. *d,l*- and *meso*-1-(2-Difluoromethylidenecyclopentyl)-2-difluoromethylidenecyclopentane (***d,l*-131**, ***meso*-131**) in $CDCl_3$.

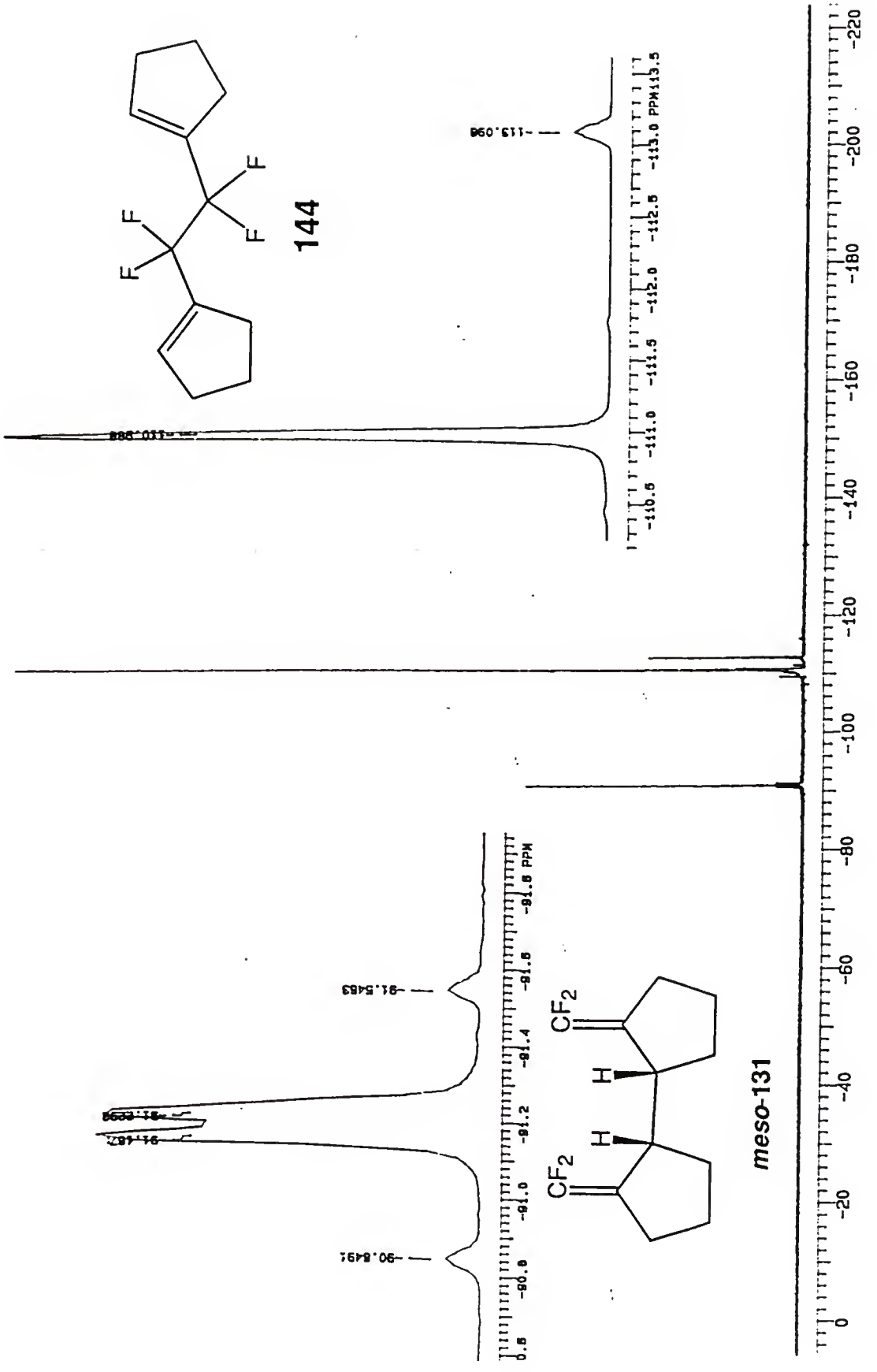


Figure B-25. Thermolysis of *meso*-1-(2-Difluoromethylidenecyclopentyl)-2-difluoromethylidenecyclopentane (***meso*-131**) Sample Containing 1-(2-(1-Cyclopentyl)-1,1,2,2-tetrafluoroethyl)cyclopentene (**144**) and C_6H_5F (113.1 ppm) in *n*-Dodecane.

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BIOGRAPHICAL SKETCH

Keith Winfield Palmer was born September 17, 1966, in Gainesville, Florida. The first few years of his life were spent feeding marshmallows to the alligators residing in Lake Alice. For fear of loss of limb, his parents decided a move to New York was in order. Keith spent the next ten years of his life growing up in rural Knox, New York, where he was "joined" by his three sisters. In 1979, the family moved to Vancouver, Washington. Witnessing the eruption of Mount St. Helens mere months after spending a vacation snowmobiling on those very slopes was both awe-inspiring and eerie. In 1981, the family moved to Midland, Michigan, for two years and then to Edwardsville, Illinois, in 1983. Here Keith began his college career at Southern Illinois University at Edwardsville with interests in biology and genetics. In 1985, the family moved to Anoka, Minnesota, and Keith continued his education at the University of Minnesota, Minneapolis. Chemistry became a fascination, and Keith spent his last two years involved in undergraduate research in organic chemistry with Professor Wayland E. Noland and received his B.S. in chemistry in July, 1988. Keith returned to Gainesville in August, 1988, to begin graduate studies in chemistry at the University of Florida. Running past Lake Alice one evening, Keith came upon an old gator with a sweet tooth which hadn't been satisfied in the past 20 years. Luckily, the gator did not hold a grudge and Keith decided to stay in Gainesville and carry out graduate research with Professor William R. Dolbier, Jr. Upon completion of his doctoral studies, Keith looks forward to working for Du Pont Polymers in Wilmington, Delaware.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

William R. Dolbier, Jr., Chairman
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

William M. Jones
Distinguished Service Professor

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Kirk S. Schanze
Associate Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Robert J. Hanrahan
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Cliff Johnston
Associate Professor of Soil Science

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

May, 1993

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